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**CLAIMS**

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**(57) [Claim(s)]**

[Claim 1] The semiconductor device which comes to have two or more electrodes which consist of one or more sorts of ingredients chosen from the group which consists of the platinum and gold which touch a fullerene thin film and this, silver, copper, aluminum, an indium, the tin oxide, indium oxide, a zinc oxide, and carbon, and is characterized by at least one electrode being an aluminum electrode.

[Claim 2] The semiconductor device according to claim 1 characterized by a fullerene thin film being a thin film which consists of carbon clusters.

[Claim 3] The semiconductor device according to claim 1 or 2 characterized by a fullerene thin film being a thin film which consists of a carbon cluster C60 and/or a carbon cluster C70.

[Claim 4] The semiconductor device according to claim 1 to 3 characterized by being one or more sorts chosen from the group which a fullerene thin film becomes from the vacuum deposition film, the cast film, and the polymer distribution film.

[Claim 5] The semiconductor device according to claim 1 to 4 to which an aluminum electrode is characterized by having an aluminum oxide layer in an interface with a fullerene thin film.

[Claim 6] The semiconductor device according to claim 1 to 5 to which an electrode is characterized by being a gap electrode or a sandwiches electrode.

[Claim 7] The semiconductor device according to claim 1 to 6 to which a semiconductor device is characterized by being a rectifying device.

[Claim 8] The semiconductor device according to claim 1 to 6 to which a semiconductor device is characterized by being a photosensor.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]** Especially this invention relates to the semiconductor device which has the outstanding rectifying action and the outstanding photoconductivity with respect to an organic-semiconductor component.

**[0002]**

**[Description of the Prior Art]** In the field of a semiconductor device, inorganic substances, such as sulfuration cadmium NIUMU, a zinc oxide, crystal silicon, an amorphous silicon, and gallium arsenide, have been used conventionally. These are used for a transistor, a rectifying device, IC and LSI, the photosensor, the solar battery, etc. However, in order to produce a semiconductor device using these inorganic substances, it was what advanced vacuum devices, an advanced film production technique, advanced purity regulation, etc. are required, and cannot be released easily.

**[0003]** On the other hand, the versatility of the organic substance, semi-conductor nature, etc. began to attract attention, and great research has been made about the semi-conductor nature of organic compounds, such as polyacethylene, polypyrrole, and a phthalocyanine, and conductivity ("new and a conductive polymer", \*\*\*\* Hiroyuki editorial supervision, CMC, (1987)). As a semiconductor device which comes to pinch a conductive polymer or an organic semiconductor with a metal especially Polyacethylene, the poly diacetylene, polypyrrole, alpha-sesquithienyl, MS component which comes to pinch semi-conductor thin films (S), such as a phthalocyanine, with a metal electrode (M), or many components, such as an MIS component which comes to pinch the thin film (I) of an insulator in between, are proposed ("Physics of Semiconductor Devices" — 2nd(s) Edition, S.M.Sze, John Wiley & Sons, NY (1981), D.Fichou, F.Garnier et al., CHEMTRONICS, 1988 or 176 pages. These organic compounds show the semi-conductor nature of P type or N type, and when it pinches with the small electrode of a work function, and the large electrode of a work function, they show a rectifying action. For example, in the case of alpha-sesquithienyl (D. Fichou, F.Garnier et al., CHEMTRONICS, 1988 or 176 pages), when this is pinched with aluminum and an indium-tin-oxide (or gold) electrode, \*\*1V show the rectifying action of 100 times or more. Furthermore, the example (Pt| polypyrrole | poly thiophene |In, M.Aizawa, H.Shirakawa, Synth.Met., No. 18, and 711 pages (1987)) which built the rectifying device, and the example (H. Koezuka, et al., Synth.Met., No. 18, and 699 pages (1987)) which built FET are also known for junction of a different-species conductive polymer. Moreover, a phthalocyanine etc. shows a photoconductivity, the application to a solar battery etc. is considered, and the solar battery pinched with aluminum and ITO glass (electrically conductive glass by the indium oxide - tin-oxide thin film) is examined.

**[0004]**

**[Problem(s) to be Solved by the Invention]** the above-mentioned organic compound — general — the instability (the air in polyacethylene —) of S layers, i.e., a conductive polymer layer, or an organic-semiconductor layer the fall (alpha-sesquithienyl —) of repeatability by mixing of an impurity, such as instability over humidity etc., and instability after doping A phthalocyanine etc. does not have the solvent which dissolves only concentrated-sulfuric-acid extent, and

improvement in purity is very difficult for it. Indeterminacy at the time of component formation (mixing of the catalyst by the vapor phase polymerization, electrolytic polymerization, etc., an electrolyte, etc.) Mixing of the impurity by the pyrolysis at the time of vacuum deposition, such as alpha-sesquithienyl and a phthalocyanine, Neither has resulted in utilization by the corrosion (corrosion of the electrode by the dopant, promotion of oxidization of an aluminum electrode which is looked at by the phthalocyanine, etc.) of the electrode after component formation, the mechanical brittleness (if vacuum deposition film, such as alpha-sesquithienyl and a phthalocyanine, is rubbed, it will separate) of a thin film, etc. Furthermore in a solar battery, it has not resulted [ from the lowness of conversion efficiency ] in the degradation with the passage of time and utilization. It is electrophotography photo conductor extent using the polymer battery which used the poly aniline, the capacitor using TCNQ, a phthalocyanine, etc. which was slightly put in practical use with the organic substance, and the present condition is that an outstanding result cannot be found.

[0005]

[Means for Solving the Problem] this invention persons take an example by the various faults like the above of organic semiconductors including the conventional conductive polymer. As a result of inquiring wholeheartedly that these should be improved, a fullerene thin film is used. While forming from one or more sorts of ingredients chosen from the group which prepares two or more electrodes so that this may be touched, and consists this electrode of platinum, gold, silver, copper, aluminum, an indium, the tin oxide, indium oxide, a zinc oxide, and carbon By using the at least one electrode as an aluminum electrode, a semiconductor device is easily obtained with sufficient repeatability, and it finds out that said technical problem is also solvable, and came to complete this invention.

[0006] That is, this invention comes to have two or more electrodes which consist of one or more sorts of ingredients chosen from the group which consists of the platinum and gold which touch a fullerene thin film and this, silver, copper, aluminum, an indium, the tin oxide, indium oxide, a zinc oxide, and carbon, and at least one electrode offers the semiconductor device characterized by being an aluminum electrode.

[0007] Hereafter, this invention is explained in detail. The fullerene thin film used by this invention is a thin film formed using fullerene. here, it becomes fullerene from sp<sup>2</sup> carbon — it is the generic name of the carbon cluster of the shape of spherical or a Rugby ball, and, generally C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, and C<sub>84</sub> grade are known. These contain carbon in arc discharge or the middle class of soot which carry out resistance heating, and it was made to evaporate, it quenched with inert gas, such as helium, and was generated, and C<sub>60</sub> (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) contains them. [ most ] And the mixture of the above-mentioned carbon cluster is obtained from this soot by extracting, for example with solvents, such as a hexane, benzene, toluene, a mesitylene, and a carbon disulfide. for refining this mixture furthermore and isolating respectively — usually — purification of an organic compound — business — \*\*\*\* — a chromatography — technique (for example, Nature (s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) can be used. In this invention, the mixed fullerene by which composition and isolation perform extract and insoluble impurity removal, and are acquired from the soot containing C<sub>60</sub> or C<sub>70</sub>, or these is used preferably.

[ easy ]

[0008] A fullerene thin film can be formed by various kinds of film production approaches, and can be used, for example, the vacuum deposition film, the cast film, the polymer distribution film, etc. can be used. According to the technique of general vacuum deposition, fullerene is heated under the vacuum of 5x10 to 5 or less torrs using a metallicity boat or an alumina nature boat (the volume thin film handbooks and for 131st committee of the Japan Society for the Promotion of Science thin film, Ohm-Sha (1984), etc.), and the vacuum deposition film can form a thin film by putting a substrate on the upper part or lower part. Under the present circumstances, the need may be accepted, and a substrate may be heated or cooled. When a thin film is amorphous when a substrate is cooled, and it heats more than a room temperature or it, it is obtained as a crystallized state. The vacuum deposition film of these fullerene is very firmly [ stably ] firm in air. For example, the conventional phthalocyanine, alpha-sesquithienyl, etc. will separate, if it

rubs, and to being inferior to a mechanical strength so that it can exfoliate easily with a Scotch tape etc., even if it rubs the vacuum evaporation film of fullerene, it does not separate easily, but it is firm film which cannot exfoliate and is excellent in a Scotch tape at a mechanical strength.

[0009] The cast film is the means which uses the property which for example, fullerene dissolves in aromatic hydrocarbon, such as benzene, toluene, and a mesitylene, a carbon disulfide, n-hexane, etc., and can create a thin film simple. Namely, make it dissolve in the above-mentioned solvent etc., and it is dropped on a substrate, or a substrate is fixed on a spinner. After the above-mentioned solution is dropped, make it rotate at a suitable rotational frequency, and thin-film-ize a spinner. Or with the means of thin-film-izing the solution dropped on the substrate using a bar coating machine or a doctor blade, it can thin-film-ize and, subsequently a film can be produced air drying, heat, or by drying with means, such as carrying out a vacuum drying.

[0010] The polymer distribution film can be produced with the same means as the above-mentioned cast film, after adding fullerene in the solution of a polymer and making it dissolve or distribute. As the distributed approach, the pigment-content powder technique, such as a paint shaker, a spec. SUMIKI sir mill, a sand mill, a ball mill, ATORATA, and a kneader, can be used. As a polymer which can be used here, although there is especially no limit, when an example is given, there are copolymers, such as fluorination polymers, such as vinyl system polymers, such as saturated polyester, unsaturated polyester, a polycarbonate, a polyvinyl chloride, Pori acetic-acid vinyl, a poly vinyl carbazole, and styrene, fluoride poly vinylidene, and fluoride polyvinyl, and a styrene maleic acid, etc. Moreover, for example, liquid crystal macromolecules, such as a polyacrylate system liquid crystal macromolecule and a polysiloxane system liquid crystal macromolecule, can also be used.

[0011] In order to pull out the semi-conductor nature which was excellent in fullerene, it is required to prepare two or more electrodes which touch a fullerene thin film. What consists of one or more sorts of ingredients chosen from the small aluminum of a work function or the large platinum of a work function, gold, silver, copper, an indium, the tin oxide (for example, Nesa glass), indium oxide, indium oxide - the tin oxide (for example, ITO glass), a zinc oxide, and carbon (graphite, glassy carbon) as an electrode is used, and let especially at least one of the electrodes of these be an aluminum electrode. When using as a semiconductor device especially a transistor, a rectifying device, etc., it is necessary to prepare the small electrode of the above-mentioned work function, and the large electrode of a work function. However, if an aluminum electrode is used, especially, a semiconductor device can show a bidirectional rectifying action and can use it as a bidirectional switching element, a bidirectional rectifying device, etc. Furthermore, if this electrode is put to air after forming an aluminum electrode, a very thin aluminum oxide layer will be formed in a front face. The component of this invention constituted by forming a fullerene thin film besides and subsequently forming the electrode of arbitration also shows a higher rectification ratio, and will become still more desirable as a rectifying device. Moreover, also when using as a photosensor, a big photocurrent can be acquired by using what was mentioned above as an electrode and using aluminum for each other electrode or one electrode. Especially with the component which formed and obtained the aluminum oxide layer to the interface of an electrode and a fullerene thin film like the above, a still bigger photocurrent can be acquired and it will become desirable.

[0012] A metal plate, a carbon plate, a thin film, the conductive paint film, etc. can be used for an electrode with any gestalt. When using it with the gestalt of a thin film, it can be used with the means of a metallic foil, the vacuum evaporation film, the sputtering film, an electrodeposited film, the spray pyrolysis film, etc., thin-film-izing. Moreover, a conductive paint (for example, silver, a carbon content coating) can be applied, and an electrode can also be formed. Here, when preparing an electrode by film production or spreading, a semiconductor device is preferably formed using a substrate. As this substrate, there is especially no limit and it should just be an insulating thing. Moreover, especially when using tabular electrodes, such as a metal plate and a carbon plate, it is not necessary to use a substrate.

[0013] As a configuration of an electrode, gap electrodes, such as a parallel pole or a gear-tooth electrode of a comb, or the sandwiches electrode prepared so that a fullerene thin film may be

pinched can be used, for example. Thickness of an electrode can be made arbitrary, when using it as a semiconductor device, especially a rectifying device, or when using it as a photosensor with a gap electrode. Moreover, although especially a limit does not have the gap width of face of a gap electrode, since a current will become small if gap width of face is large, the gap of 1mm or less is desirable. Moreover, since a current value becomes [ the longer one ] large and a big response is obtained, gap length is suitable. Also in a gap electrode, if the gear-tooth electrode of a comb is used, since gap length can do it still longer, it is more desirable. On the other hand, when using it as a photosensor with a sandwiches electrode, the electrode of the side which carries out incidence of the light needs to be translucent. Although the range whose permeability of light is 98% - 0.1% is used when using an oxide electrode, the responsibility over light has the high one where the permeability of light is larger. In the case of a metal electrode, the responsibility over light has the high one where the permeability of light is larger, but if permeability is too large, an electrode will not conduct a current. Therefore, as for the permeability of light, 50% - 0.1% of range is used suitably.

[0014] Moreover, about the thickness of the fullerene thin film which constitutes a semiconductor device, when using a gap electrode, that there should just be thickness of at least 1 molecule, it can use in 10A - 100 micrometers, and especially the range of 10A - 10 micrometers is used especially suitably. Since each other electrode will short-circuit if too thin when using a sandwiches electrode, a certain amount of thickness is required. In this case, the range of 100A - 100 micrometers is suitable for the thickness of a fullerene thin film, and it is especially formed in 200A - 10 micrometers preferably.

[0015] The semiconductor device of this invention constituted using a fullerene thin film and an electrode which were explained above is explained using a drawing. Each drawing 1 -4 shows an example of the semiconductor device of this invention. Each of drawing 1 and drawing 2 is what showed an example of a semiconductor device and a circuit which used the gap electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). For an insulating substrate, 2a, and 2b, as for a fullerene thin film and 4, an electrode and 3 are [ the sign 1 in drawing / DC power supply and 5 ] ammeters. The semiconductor device shown in drawing 1 is prepared so that gear-tooth electrode 2a of two combs and 2b may have few gaps and may gear on an insulating substrate 1, and the fullerene thin film 3 is further formed in the top face. Moreover, electrode 2a and 2b are connected through DC power supply 4 and an ammeter 5. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for the fullerene thin film 3 if needed. Or the fullerene thin film 3 can be formed on an insulating substrate 1 like drawing 2 (b), and it can also consider as the configuration which prepared gear-tooth electrode 2a of a comb, and 2b in the top face further. The semiconductor device using such a gap electrode can be suitably used as a photosensor, it is in the condition which impressed electric field to electrode 2a and 2b from the power source 4, and if light is irradiated by the fullerene thin film 3, the current value between electrode 2a and 2b will change. This amount of current value changes is detected by the ammeter 5, and can measure the optical reinforcement irradiated based on this.

[0016] The semiconductor device of this invention which used the gap electrode for drawing 2 , and other examples of a circuit are shown. The fullerene thin film 3 is formed on an insulating substrate 1, and, as for the semiconductor device of this example, two parallel-pole 2a and 2bs are prepared in that top face. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for electrode 2a, 2b, and the fullerene thin film 3 if needed. Or parallel-pole 2a and 2b can be prepared on an insulating substrate 1 like drawing 1 (b), and it can also consider as the configuration in which the fullerene thin film 3 was formed on the top face.

[0017] Drawing 3 and drawing 4 are what showed the example of the semiconductor device which used the sandwiches electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). The 1st three electrode 2a, 2a, and 2a with which the semiconductor device shown in drawing 3 was formed in the shape of a strip of paper on the insulating substrate 1 is formed in parallel. It is prepared so that the 1st electrode 2a, 2a, and 2a of the above, and 2nd three electrode 2b, 2b and 2b which the fullerene thin film 3 was formed in

the insulating substrate 1 and the top face of these 1st electrodes 2a, 2a, and 2a, and were further formed in the shape of a strip of paper on this fullerene thin film 3 may cross at right angles in parallel. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for the 2nd electrode 2b, 2b, 2b, and fullerene thin film 3 if needed. Here, the number of the 1st electrode and the 2nd electrodes is set as the number of one or more arbitration, respectively, and can carry out things. The semiconductor device using such a sandwiches electrode is used suitable for the integrated rectifying devices (for example, switching element etc.), for example, can drive liquid crystal, ECD, etc. Or it is suitably used also as photosensors (for example, image sensors etc.). Electric field can be impressed to the 1st electrode and 2nd electrode which go direct mutually from an outdrive unit (not shown) in these cases, and it can use as a rectifying device or a photosensor.

[0018] Drawing 4 shows other examples of the semiconductor device of this invention which used the sandwiches electrode. 2nd electrode 2b is prepared on an insulating substrate 1, all over the this insulating-substrate 1 and 2nd electrode 2b top, the fullerene thin film 3 is formed and, as for this thing, the 1st electrode 2a, 2a, and 2a formed in the shape of a strip of paper on the fullerene thin film 3 is formed further. The number of these 1st electrode 2a is set as the number of one or more arbitration, and can carry out things. In addition, what kind of configurations, such as not only the shape of a strip of paper but a circle, an ellipse, etc., are sufficient as 1st electrode 2a. 2nd electrode 2b leaves one edge section 1a of substrate 1 top face, and is formed in band-like [ thick ]. Moreover, the 1st electrode 2a, 2a, and 2a It intersects perpendicularly with the longitudinal direction of 2nd electrode 2b formed previously, it is prepared so that it may be crossed and located on edge section 1a of the above-mentioned insulating substrate 1 from on 2nd [ of a parenthesis ] electrode 2b, and it can prevent un-arranging [ which wiring from the 1st electrode and 2nd electrode short-circuits by this ]. Moreover, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed if needed on the 1st electrode 2a, 2a, and 2a and the fullerene thin film 3. Thus, the constituted semiconductor device can be used effective in an independent rectifying device, a transistor, a photosensor, etc.

[0019] In addition, the semiconductor device of this invention is not limited to the configuration of the above-mentioned example, and various gestalten are possible for it and it may consist of a crystal, powder, etc. Furthermore, various gestalten can be taken by the purpose of using a semi-conductor, and based on these purposes, the configuration of an electrode and a component is changed suitably and it deals in it.

[0020]

[Example] (Example 1 of reference)

The semiconductor device which has the configuration shown in drawing 1 was produced. On slide glass 1, gear-tooth electrode 2a of a comb with gap width of face of 0.10mm, ten electrode overlap, and an electrode overall length of 50mm and 2b were formed with vacuum deposition. Gold was used for electrode 2a and 2b, and it stuck to the thickness of 500Å under the vacuum of  $5 \times 10^{-5}$  torr. The slide glass 1 in which this electrode 2a and 2b were formed was put on 20cm on the alumina crucible of a vacuum deposition machine, and it vapor-deposited, having put the carbon cluster C60 into the crucible made from an alumina, and heating at 520–550 degrees C under the vacuum of  $5 \times 10^{-6}$  torr (5Å/(second)), the vacuum deposition film 3 of C60 was stuck to the thickness of 300Å, and the semiconductor device was produced. They are wavelength;400nm and optical on-the-strength;7 mW/cm<sup>2</sup>, impressing the electric field of 10V to this component. When the homogeneous light was irradiated, the photocurrent of 55pA was detected. It is optical reinforcement 0.1, 0.5, 1.0 and 2.0, and 5.0 mW/cm<sup>2</sup> When it was made to change, the photocurrent also increased along with the increment in optical reinforcement. Subsequently, although this component was left for one month in atmospheric air, it was changeless to a photocurrent. Moreover, although the Scotch tape was stretched on the vacuum deposition film of C60 and subsequently being removed, C60 vacuum-deposition film has arrived at the substrate firmly, and did not separate. Furthermore, although the epoxy resin performed the protection coat on the front face of this component, it was almost changeless to a photocurrent. Therefore, the component obtained in this example of reference had the engine

performance which was excellent as a photosensor.

[0021] (Example 1 of a comparison)

Like the above-mentioned example 1 of reference, on electrode 2a formed on slide glass 1, and 2b, vacuum deposition of the non-metal phthalocyanine was similarly carried out instead of the carbon cluster C60, and the thin film 3 was formed. When the same homogeneous light as the example 1 of reference was irradiated, the photocurrent of 15nA was observed. However, when this component was left for one month in atmospheric air, the photocurrent fell clearly.

Moreover, when the Scotch tape was stuck and having been stripped on the non-metal phthalocyanine vacuum evaporation film, the thin film of a non-metal phthalocyanine peeled altogether with the Scotch tape. Furthermore, when a protection coat is carried out with an epoxy resin, most photocurrents are no longer observed by the fatal thing.

[0022] (Example 1)

In the example 1 of reference, the semiconductor device was similarly produced as electrode 2a and 2b except using aluminum instead of gold. When the homogeneous light as well as the example 1 of reference was irradiated, the photocurrent of 600pA was observed. The photocurrent was observed even if it changed the wavelength of the homogeneous light with 300,500,600,700nm. Therefore, it was admitted that this component could detect a photocurrent in a visible region from ultraviolet. Furthermore, when applied voltage was set to 100V, it was admitted by a photocurrent's becoming 10 times and impressing large electric field that an optical large response was obtained.

[0023]

[0024] (Example 2)

The semiconductor device was produced in the above-mentioned example 1, using the cast film as a fullerene thin film 3. Like the example 1, using the spinner, the liquid made to dissolve the carbon cluster C60 in toluene was dropped, the cast film 3 of C60 was produced, the vacuum drying was carried out and the semiconductor device was produced at 100 more degrees C for 1 hour on electrode 2a which vapor-deposited aluminum on slide glass 1, and 2b. 1V are impressed to this component and they are 400nm and 5 mW/cm<sup>2</sup>. When the homogeneous light was irradiated, the photocurrent of 425pA was observed.

[0025] (Example 3)

The semiconductor device which has the configuration shown in drawing 4 was produced. Width of face of 0.5cm and die length of 3cm were etched with the hydrochloric acid on 3cm 2cmx indium tin glass (ITO glass) 1, the conductive film was removed (part equivalent to 1in drawing 4 a), and the conductive remaining film was made into indium oxide (ITO) electrode 2b. On this electrode 2b, the polymer distribution film 3 of C60 was produced for the dispersion liquid (60; 20mg of C, vinyl acetate; 20mg, ethyl acetate; dispersion liquid which put the glass bead into 200mg and were distributed with the paint shaker for 1 hour) which made vinyl acetate / ethyl-acetate solution distribute C60 using bar coating-machine #10. The vacuum drying of this film 3 was carried out at 100 degrees C for 1 hour. Thickness was 1 micrometer. Subsequently, aluminum (width-of-face [ of 0.5cm ], die length of 1.5cm) electrode 2a was formed with three pieces and vacuum deposition on this film 3. From the function generator, the triangular wave of -2V to +2V was impressed at a scanning speed of 0.001Hz between this indium oxide electrode 2b and aluminum electrode 2a. The current-voltage characteristic at this time was shown in drawing 5. The rectifying action was shown so that clearly from drawing 5. On this component, although 3 sets of electrodes were formed, the repeatability was good. Moreover, even if it carried out the protection coat of the whole with the epoxy resin, the current-voltage characteristic hardly changed. Therefore, it was admitted that this component was an outstanding rectifying device.

[0026] (Example 4)

In the above-mentioned example 3, except having replaced with the indium oxide electrode and having prepared tin-oxide electrode 2b by using NESA glass instead of ITO glass, when the semiconductor device was produced similarly, this thing showed the good rectifying action like the thing of an example 3.

[0027] (Example 2 of a comparison)



In the above-mentioned example 3, the semiconductor device was similarly formed except using a non-metal phthalocyanine instead of C60. Also in this case, the rectifying action was shown similarly. However, when a protection coat was carried out with an epoxy resin, the rectifying action decreased greatly.

[0028] (Example 5)

The semiconductor device which has the configuration shown in drawing 4 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, and on this substrate 1, vacuum deposition of the aluminum was carried out to the thickness of a 200 Å to 1000 Å, and it considered as electrode 2b (permeability of the 400nm homogeneous light; 2.18%). Furthermore, on this, vacuum deposition of C60 was carried out to 1000 Å thickness like the example 1 of reference, and the vacuum deposition film 3 of C60 was formed. Subsequently, on it, vacuum deposition of the two 0.5cmx1.5cm aluminum electrodes was carried out, and the semiconductor device was formed. When the triangular wave which is -1V to +1V was impressed to this component from the function generator (scanning speed; 0.002Hz), the current-voltage characteristic showed the bidirectional rectifying action as shown in drawing 6. Moreover, repeatability was good about three electrodes.

[0029] (Example 3 of a comparison)

2000 Å of alpha-sesquithienyls was vapor-deposited on the top face of the glass plate 1 in which aluminum electrode 2b was formed, like the example 5 (20 Å/(second)). If it is very hard to vapor-deposit alpha-sesquithienyl and it is vapor-deposited slowly, it will serve as film which decomposed and contained many impurities. Although decomposition will decrease if it vapor-deposits quickly (20 Å/(second) or more), an impurity is contained too. Subsequently, 0.5cmx1.5cm aluminum electrode 2a was prepared by three-piece vacuum evaporation. The triangular wave of -2 to +2V was impressed to this component from the function generator (0.002Hz). This component showed a rectifying action, or did not show it, and its repeatability was very bad.

[0030] (Example 6)

The homogeneous light of wavelength;400nm and on-the-strength;700 microwatt/cm<sup>2</sup> was irradiated from the glass plate 1 side at the electrode, impressing 0.1V to aluminum electrode 2a of the semiconductor device obtained in the example 5, and 2b. The photocurrent of 535nA was observed at this time. When changing the wavelength of exposure light, the photocurrent has been observed to the 800nm homogeneous light. Moreover, by the homogeneous light with a wavelength of 400nm, when changing optical reinforcement, the photocurrent also increased according to exposure light reinforcement. Moreover, repeatability was good about three electrodes.

[0031] (Example 7)

The semiconductor device which has the configuration shown in drawing 4 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, on this substrate 1, platinum was stuck by sputtering and platinum-electrode 2b was formed. Subsequently, the polycarbonate polymer distribution film 3 of C60 was formed with the spinner, and it dried. Subsequently, aluminum electrode 2a was formed with vacuum deposition. The rectifying action was observed when the triangular wave of +1V was impressed from -1 like the example 5.

[0032] (Example 8)

When the platinum vacuum evaporation film was replaced with the carbon-shadowing film in the above-mentioned example 7 and carbon-electrode 2b was prepared, the rectifying action was shown similarly.

[0033] (Example 9)

In the above-mentioned example 5, except using C70 instead of C60, similarly, when the semiconductor device was obtained and measured, the current-voltage characteristic showed the same bidirectional rectifying characteristic.

[0034] (Example 10)

In the example 7, silver electrode 2b was formed with vacuum deposition instead of the platinum electrode. This component showed the rectifying action like drawing 5 similarly. Moreover, the photocurrent was observed when on-the-strength 1 mW/cm<sup>2</sup> and the 450nm homogeneous light

were irradiated from an aluminum electrode side.

[0035] (Example 11)

In the example 7, copper-electrode 2b was formed with vacuum deposition instead of the platinum electrode. This component showed the rectifying action like drawing 5 similarly. Moreover, the photocurrent was observed when on-the-strength 1 mW/cm<sup>2</sup> and the 450nm homogeneous light were irradiated from an aluminum electrode side.

[0036] (Example 12)

In the example 3, instead of ITO glass and an indium oxide electrode, when others were performed like the example 3 using what formed zinc-oxide electrode 2b by sputtering on the glass substrate 1, the same rectifying action was observed.

[0037] (Example 13)

The same component as an example 5 was formed. First, after forming aluminum electrode 2b on a substrate, it once took out in air and was left under the room temperature for 24 hours. Then, it put in in the vacuum evaporation system, vacuum deposition of C60 was carried out to 1000Å thickness like the example 5, and the vacuum deposition film 3 of C60 was formed. Then, two pieces were vapor-deposited for 0.5cmx1.5cm aluminum electrode 2a, one piece was vapor-deposited for the golden electrode, respectively, and the semiconductor device was formed. The permeability of electrode 2a (aluminum, gold) and 400nm homogeneous light of 2b was 2%. After component formation, also when the current-voltage characteristic of -1+1V was measured immediately, and electrode 2a was any of aluminum and gold, a rectifying characteristic like drawing 5 was shown. Moreover, when 1V were impressed between electrode 2a and 2b, 2 was irradiated at aluminum electrode 2b and the homogeneous light was irradiated at the wavelength of 400nm on the strength of 5mW/cm, as compared with the time of irradiating the same light as aluminum electrode 2a or golden electrode 2a, the about 25 times as many photocurrent as this was observed. When argon etching of this component was carried out from the electrode 2a side using ESCA and the presentation of the membranous thickness direction was analyzed, it was admitted that the aluminum oxide existed in the interface of C60 film 3 and aluminum electrode 2b.

[0038] (Example 2 of reference)

Commercial crude soot was refined and C60 and C70 were obtained. First, 4g (vacuum metallurgy incorporated company make) of crude soot containing fullerene was put into the extraction thimble, and it extracted by n-hexane;200ml for 24 hours using the Soxhlet extractor. Subsequently, the solvent was changed into mesitylene;200ml and the extract was performed for further 24 hours. When the first n-hexane solution was analyzed by liquid chromatography (silica gel - n-hexane), the ratio of C60:C70 is 9:1 and did not contain most of 70 or more C fullerene. The ratio of C60:C70 is about 6:4, and the mesitylene extract was carrying out variety content of the 70 or more C fullerene. n-hexane extract was condensed by the evaporator and 0.26g fullerene mixture was obtained. Using the ODS column, the mixed solvent of a 2-propanol / toluene;6/4 was used as the developing solution, and 0.21g and 0.02g of high grades C70 were obtained for the high grade C60 using inside low voltage preparative chromatograph. The mesitylene extract was condensed by the evaporator and mixed fullerene 0.13g was obtained. It isolated preparatively by the chromatograph similarly and mixture;0.01g of 60; 0.07g of high grades C, 70; 0.04g of high grades C, and other fullerene was obtained. Mixture contained C76, C78, C84, and fullerene with still larger molecular weight from GC-MS analysis.

[0039]

[Effect of the Invention] As explained above, the semiconductor device of this invention comes to have two or more electrodes which touch a fullerene thin film and this, and at least one electrode consists of small aluminum electrodes of a work function. Therefore, when especially two electrodes consist of aluminum, a bidirectional rectifying action can be shown and it can be used as a bidirectional switching element, a bidirectional rectifying device, etc. moreover, when a very thin aluminum oxide layer is formed in the aluminum electrode surface which touches C60 interface A bigger photocurrent can be acquired, also when a higher rectification ratio is shown and it uses as a photosensor further (for example, in the example 1, photocurrent 600pA of 10 times or more was obtained [ photocurrent 55pA obtained when gold was used for the two

electrodes made into the example 1 of reference ].). The outstanding engine performance is shown. Moreover, this semiconductor device shows semi-conductor nature especially a rectifying action, and a photoconductivity. And fullerene is easy to compound, and in order to dissolve in a solvent, it is easy to refine, and it can obtain a high grade article easily. Moreover, thermal resistance is also high, since the decomposition at the time of vacuum evaporation does not take place, either, component-izing is easy and a property with sufficient repeatability is acquired. Moreover, it can be used also in the form of the cast film which does not need a vacuum, and the polymer distribution film. Therefore, the semiconductor device which is rich in stability and repeatability can be easily constituted by using the fullerene thin film which produces fullerene and is obtained. Furthermore, since the engine performance does not change even if it gives the protection coat which used resin etc., the semiconductor device of this invention can be used for an extensive application. Especially, it is broadly applicable to driver elements, such as a rectifying device, liquid crystal using a rectifying action, and an ECD component, a photosensor, or the image sensors adapting a photosensor function.

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**TECHNICAL FIELD**

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[Industrial Application] Especially this invention relates to the semiconductor device which has the outstanding rectifying action and the outstanding photoconductivity with respect to an organic-semiconductor component.

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**PRIOR ART**

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[Description of the Prior Art] In the field of a semiconductor device, inorganic substances, such as sulfuration cadmium NIUMU, a zinc oxide, crystal silicon, an amorphous silicon, and gallium arsenide, have been used conventionally. These are used for a transistor, a rectifying device, IC and LSI, the photosensor, the solar battery, etc. However, in order to produce a semiconductor device using these inorganic substances, it was what advanced vacuum devices, an advanced film production technique, advanced purity regulation, etc. are required, and cannot be released easily.

[0003] On the other hand, the versatility of the organic substance, semi-conductor nature, etc. began to attract attention, and great research has been made about the semi-conductor nature of organic compounds, such as polyacethylene, polypyrrole, and a phthalocyanine, and conductivity ("new and a conductive polymer", \*\*\*\* Hiroyuki editorial supervision, CMC, (1987)). As a semiconductor device which comes to pinch a conductive polymer or an organic semiconductor with a metal especially Polyacethylene, the poly diacethylene, polypyrrole, alpha-sesquithienyl, MS component which comes to pinch semi-conductor thin films (S), such as a phthalocyanine, with a metal electrode (M), or many components, such as an MIS component which comes to pinch the thin film (I) of an insulator in between, are proposed ("Physics of Semiconductor Devices" —) 2nd(s) Edition, S.M.Sze, John Wiley & Sons, NY (1981), D.Fichou, F.Garnier et al., CHEMTRONICS, 1988 or 176 pages. These organic compounds show the semi-conductor nature of P type or N type, and when it pinches with the small electrode of a work function, and the large electrode of a work function, they show a rectifying action. For example, in the case of alpha-sesquithienyl (D. Fichou, F.Garnier et al., CHEMTRONICS, 1988 or 176 pages), when this is pinched with aluminum and an indium-tin-oxide (or gold) electrode, \*\*1V show the rectifying action of 100 times or more. Furthermore, the example (Pt| polypyrrole | poly thiophene |In, M.Aizawa, H.Shirakawa, Synth.Met., No. 18, and 711 pages (1987)) which built the rectifying device, and the example (H. Koezuka, et al., Synth.Met., No. 18, and 699 pages (1987)) which built FET are also known for junction of a different-species conductive polymer. Moreover, a phthalocyanine etc. shows a photoconductivity, the application to a solar battery etc. is considered, and the solar battery pinched with aluminum and ITO glass (electrically conductive glass by the indium oxide - tin-oxide thin film) is examined.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As explained above, the semiconductor device of this invention comes to have two or more electrodes which touch a fullerene thin film and this, and at least one electrode consists of small aluminum electrodes of a work function. Therefore, when especially two electrodes consist of aluminum, a bidirectional rectifying action can be shown and it can be used as a bidirectional switching element, a bidirectional rectifying device, etc. moreover, when a very thin aluminum oxide layer is formed in the aluminum electrode surface which touches C60 interface A bigger photocurrent can be acquired, also when a higher rectification ratio is shown and it uses as a photosensor further (for example, in the example 1, photocurrent 600pA of 10 times or more was obtained [ photocurrent 55pA obtained when gold was used for the two electrodes made into the example 1 of reference ]). The outstanding engine performance is shown. Moreover, this semiconductor device shows semi-conductor nature especially a rectifying action, and a photoconductivity. And fullerene is easy to compound, and in order to dissolve in a solvent, it is easy to refine, and it can obtain a high grade article easily. Moreover, thermal resistance is also high, since the decomposition at the time of vacuum evaporations does not take place, either, component-izing is easy and a property with sufficient repeatability is acquired. Moreover, it can be used also in the form of the cast film which does not need a vacuum, and the polymer distribution film. Therefore, the semiconductor device which is rich in stability and repeatability can be easily constituted by using the fullerene thin film which produces fullerene and is obtained. Furthermore, since the engine performance does not change even if it gives the protection coat which used resin etc., the semiconductor device of this invention can be used for an extensive application. Especially, it is broadly applicable to driver elements, such as a rectifying device, liquid crystal using a rectifying action, and an ECD component, a photosensor, or the image sensors adapting a photosensor function.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] the above-mentioned organic compound — general — the instability (the air in polyacetylene —) of S layers, i.e., a conductive polymer layer, or an organic-semiconductor layer the fall (alpha-sesquithienyl —) of repeatability by mixing of an impurity, such as instability over humidity etc., and instability after doping A phthalocyanine etc. does not have the solvent which dissolves only concentrated-sulfuric-acid extent, and improvement in purity is very difficult for it. Indeterminacy at the time of component formation (mixing of the catalyst by the vapor phase polymerization, electrolytic polymerization, etc., an electrolyte, etc.) Mixing of the impurity by the pyrolysis at the time of vacuum deposition, such as alpha-sesquithienyl and a phthalocyanine, Neither has resulted in utilization by the corrosion (corrosion of the electrode by the dopant, promotion of oxidization of an aluminum electrode which is looked at by the phthalocyanine, etc.) of the electrode after component formation, the mechanical brittleness (if vacuum deposition film, such as alpha-sesquithienyl and a phthalocyanine, is rubbed, it will separate) of a thin film, etc. Furthermore in a solar battery, it has not resulted [ from the lowness of conversion efficiency ] in the degradation with the passage of time and utilization. It is electrophotography photo conductor extent using the polymer battery which used the poly aniline, the capacitor using TCNQ, a phthalocyanine, etc. which was slightly put in practical use with the organic substance, and the present condition is that an outstanding result cannot be found.

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**MEANS**

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[Means for Solving the Problem] this invention persons take an example by the various faults like the above of organic semiconductors including the conventional conductive polymer. As a result of inquiring wholeheartedly that these should be improved, a fullerene thin film is used. While forming from one or more sorts of ingredients chosen from the group which prepares two or more electrodes so that this may be touched, and consists this electrode of platinum, gold, silver, copper, aluminum, an indium, the tin oxide, indium oxide, a zinc oxide, and carbon By using the at least one electrode as an aluminum electrode, a semiconductor device is easily obtained with sufficient repeatability, and it finds out that said technical problem is also solvable, and came to complete this invention.

[0006] That is, this invention comes to have two or more electrodes which consist of one or more sorts of ingredients chosen from the group which consists of the platinum and gold which touch a fullerene thin film and this, silver, copper, aluminum, an indium, the tin oxide, indium oxide, a zinc oxide, and carbon, and at least one electrode offers the semiconductor device characterized by being an aluminum electrode.

[0007] Hereafter, this invention is explained in detail. The fullerene thin film used by this invention is a thin film formed using fullerene. here, it becomes fullerene from sp<sup>2</sup> carbon — it is the generic name of the carbon cluster of the shape of spherical or a Rugby ball, and, generally C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, and C<sub>84</sub> grade are known. These contain carbon in arc discharge or the middle class of soot which carry out resistance heating, and it was made to evaporate, it quenched with inert gas, such as helium, and was generated, and C<sub>60</sub> (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) contains them. [ most ] And the mixture of the above-mentioned carbon cluster is obtained from this soot by extracting, for example with solvents, such as a hexane, benzene, toluene, a mesitylene, and a carbon disulfide. for refining this mixture furthermore and isolating respectively — usually — purification of an organic compound — business — \*\*\*\* — a chromatography — technique (for example, Nature (s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) can be used. In this invention, the mixed fullerene by which composition and isolation perform extract and insoluble impurity removal, and are acquired from the soot containing C<sub>60</sub> or C<sub>70</sub>, or these is used preferably. [ easy ]

[0008] A fullerene thin film can be formed by various kinds of film production approaches, and can be used, for example, the vacuum deposition film, the cast film, the polymer distribution film, etc. can be used. According to the technique of general vacuum deposition, fullerene is heated under the vacuum of 5x10 to 5 or less torrs using a metallicity boat or an alumina nature boat (the volume thin film handbooks and for 131st committee of the Japan Society for the Promotion of Science thin film, Ohm-Sha (1984), etc.), and the vacuum deposition film can form a thin film by putting a substrate on the upper part or lower part. Under the present circumstances, the need may be accepted, and a substrate may be heated or cooled. When a thin film is amorphous when a substrate is cooled, and it heats more than a room temperature or it, it is obtained as a crystallized state. The vacuum deposition film of these fullerene is very firmly [ stably ] firm in air. For example, the conventional phthalocyanine, alpha-sesquithienyl, etc. will separate, if it rubs, and to being inferior to a mechanical strength so that it can exfoliate easily with a Scotch

tape etc., even if it rubs the vacuum evaporation film of fullerene, it does not separate easily, but it is a firm film which cannot exfoliate and is excellent in a Scotch tape at a mechanical strength.

[0009] The cast film is the means which uses the property which for example, fullerene dissolves in aromatic hydrocarbon, such as benzene, toluene, and a mesitylene, a carbon disulfide, n-hexane, etc., and can create a thin film simple. Namely, make it dissolve in the above-mentioned solvent etc., and it is dropped on a substrate, or a substrate is fixed on a spinner. After the above-mentioned solution is dropped, make it rotate at a suitable rotational frequency, and thin-film-ize a spinner. Or with the means of thin-film-izing the solution dropped on the substrate using a bar coating machine or a doctor blade, it can thin-film-ize and, subsequently a film can be produced air drying, heat, or by drying with means, such as carrying out a vacuum drying.

[0010] The polymer distribution film can be produced with the same means as the above-mentioned cast film, after adding fullerene in the solution of a polymer and making it dissolve or distribute. As the distributed approach, the pigment-content powder technique, such as a paint shaker, a spec. SUMIKI sir mill, a sand mill, a ball mill, ATORATA, and a kneader, can be used. As a polymer which can be used here, although there is especially no limit, when an example is given, there are copolymers, such as fluorination polymers, such as vinyl system polymers, such as saturated polyester, unsaturated polyester, a polycarbonate, a polyvinyl chloride, Pori acetic acid vinyl, a poly vinyl carbazole, and styrene, fluoride poly vinylidene, and fluoride polyvinyl, and a styrene maleic acid, etc. Moreover, for example, liquid crystal macromolecules, such as a polyacrylate system liquid crystal macromolecule and a polysiloxane system liquid crystal macromolecule, can also be used.

[0011] In order to pull out the semi-conductor nature which was excellent in fullerene, it is required to prepare two or more electrodes which touch a fullerene thin film. What consists of one or more sorts of ingredients chosen from the small aluminum of a work function or the large platinum of a work function, gold, silver, copper, an indium, the tin oxide (for example, Nesa glass), indium oxide, indium oxide - the tin oxide (for example, ITO glass), a zinc oxide, and carbon (graphite, glassy carbon) as an electrode is used, and let especially at least one of the electrodes of these be an aluminum electrode. When using as a semiconductor device especially a transistor, a rectifying device, etc., it is necessary to prepare the small electrode of the above-mentioned work function, and the large electrode of a work function. However, if an aluminum electrode is used, especially, a semiconductor device can show a bidirectional rectifying action and can use it as a bidirectional switching element, a bidirectional rectifying device, etc. Furthermore, if this electrode is put to air after forming an aluminum electrode, a very thin aluminum oxide layer will be formed in a front face. The component of this invention constituted by forming a fullerene thin film besides and subsequently forming the electrode of arbitration also shows a higher rectification ratio, and will become still more desirable as a rectifying device. Moreover, also when using as a photosensor, a big photocurrent can be acquired by using what was mentioned above as an electrode and using aluminum for each other electrode or one electrode. Especially with the component which formed and obtained the aluminum oxide layer to the interface of an electrode and a fullerene thin film like the above, a still bigger photocurrent can be acquired and it will become desirable.

[0012] A metal plate, a carbon plate, a thin film, the conductive paint film, etc. can be used for an electrode with any gestalt. When using it with the gestalt of a thin film, it can be used with the means of a metallic foil, the vacuum evaporation film, the sputtering film, an electrodeposited film, the spray pyrolysis film, etc., thin-film-izing. Moreover, a conductive paint (for example, silver, a carbon content coating) can be applied, and an electrode can also be formed. Here, when preparing an electrode by film production or spreading, a semiconductor device is preferably formed using a substrate. As this substrate, there is especially no limit and it should just be an insulating thing. Moreover, especially when using tabular electrodes, such as a metal plate and a carbon plate, it is not necessary to use a substrate.

[0013] As a configuration of an electrode, gap electrodes, such as a parallel pole or a gear-tooth electrode of a comb, or the sandwiches electrode prepared so that a fullerene thin film may be pinched can be used, for example. Thickness of an electrode can be made arbitrary, when using

it as a semiconductor device, especially a rectifying device, or when using it as a photosensor with a gap electrode. Moreover, although especially a limit does not have the gap width of face of a gap electrode, since a current will become small if gap width of face is large, the gap of 1mm or less is desirable. Moreover, since a current value becomes [ the longer one ] large and a big response is obtained, gap length is suitable. Also in a gap electrode, if the gear-tooth electrode of a comb is used, since gap length can do it still longer, it is more desirable. On the other hand, when using it as a photosensor with a sandwiches electrode, the electrode of the side which carries out incidence of the light needs to be translucent. Although the range whose permeability of light is 98% - 0.1% is used when using an oxide electrode, the responsibility over light has the high one where the permeability of light is larger. In the case of a metal electrode, the responsibility over light has the high one where the permeability of light is larger, but if permeability is too large, an electrode will not conduct a current. Therefore, as for the permeability of light, 50% - 0.1% of range is used suitably.

[0014] Moreover, about the thickness of the fullerene thin film which constitutes a semiconductor device, when using a gap electrode, that there should just be thickness of at least 1 molecule, it can use in 10A - 100 micrometers, and especially the range of 10A - 10 micrometers is used especially suitably. Since each other electrode will short-circuit if too thin when using a sandwiches electrode, a certain amount of thickness is required. In this case, the range of 100A - 100 micrometers is suitable for the thickness of a fullerene thin film, and it is especially formed in 200A - 10 micrometers preferably.

[0015] The semiconductor device of this invention constituted using a fullerene thin film and an electrode which were explained above is explained using a drawing. Each drawing 1 -4 shows an example of the semiconductor device of this invention. Each of drawing 1 and drawing 2 is what showed an example of a semiconductor device and a circuit which used the gap electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). For an insulating substrate, 2a, and 2b, as for a fullerene thin film and 4, an electrode and 3 are [ the sign 1 in drawing / DC power supply and 5 ] ammeters. The semiconductor device shown in drawing 1 is prepared so that gear-tooth electrode 2a of two combs and 2b may have few gaps and may gear on an insulating substrate 1, and the fullerene thin film 3 is further formed in the top face. Moreover, electrode 2a and 2b are connected through DC power supply 4 and an ammeter 5. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for the fullerene thin film 3 if needed. Or the fullerene thin film 3 can be formed on an insulating substrate 1 like drawing 2 (b), and it can also consider as the configuration which prepared gear-tooth electrode 2a of a comb, and 2b in the top face further. The semiconductor device using such a gap electrode can be suitably used as a photosensor, it is in the condition which impressed electric field to electrode 2a and 2b from the power source 4, and if light is irradiated by the fullerene thin film 3, the current value between electrode 2a and 2b will change. This amount of current value changes is detected by the ammeter 5, and can measure the optical reinforcement irradiated based on this.

[0016] The semiconductor device of this invention which used the gap electrode for drawing 2 , and other examples of a circuit are shown. The fullerene thin film 3 is formed on an insulating substrate 1, and, as for the semiconductor device of this example, two parallel-pole 2a and 2bs are prepared in that top face. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for electrode 2a, 2b, and the fullerene thin film 3 if needed. Or parallel-pole 2a and 2b can be prepared on an insulating substrate 1 like drawing 1 (b), and it can also consider as the configuration in which the fullerene thin film 3 was formed on the top face.

[0017] Drawing 3 and drawing 4 are what showed the example of the semiconductor device which used the sandwiches electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). The 1st three electrode 2a, 2a, and 2a with which the semiconductor device shown in drawing 3 was formed in the shape of a strip of paper on the insulating substrate 1 is formed in parallel. It is prepared so that the 1st electrode 2a, 2a, and 2a of the above, and 2nd three electrode 2b, 2b and 2b which the fullerene thin film 3 was formed in the insulating substrate 1 and the top face of these 1st electrodes 2a, 2a, and 2a, and were

further formed in the shape of a strip of paper on this fullerene thin film 3 may cross at right angles in parallel. Furthermore, protective coats, such as wrap insulation polymer film or an insulating metallic oxide, can also be formed for the 2nd electrode 2b, 2b, 2b, and fullerene thin film 3 if needed. Here, the number of the 1st electrode and the 2nd electrodes is set as the number of one or more arbitration, respectively, and can carry out things. The semiconductor device using such a sandwiches electrode is used suitable for the integrated rectifying devices (for example, switching element etc.), for example, can drive liquid crystal, ECD, etc. Or it is suitably used also as photosensors (for example, image sensors etc.). Electric field can be impressed to the 1st electrode and 2nd electrode which go direct mutually from an outdrive unit (not shown) in these cases, and it can use as a rectifying device or a photosensor.

[0018] Drawing 4 shows other examples of the semiconductor device of this invention which used the sandwiches electrode. 2nd electrode 2b is prepared on an insulating substrate 1, all over the this insulating-substrate 1 and 2nd electrode 2b top, the fullerene thin film 3 is formed and, as for this thing, the 1st electrode 2a, 2a, and 2a formed in the shape of a strip of paper on the fullerene thin film 3 is formed further. The number of these 1st electrode 2a is set as the number of one or more arbitration, and can carry out things. In addition, what kind of configurations, such as not only the shape of a strip of paper but a circle, an ellipse, etc., are sufficient as 1st electrode 2a. 2nd electrode 2b leaves one edge section 1a of substrate 1 top face, and is formed in band-like [ thick ]. Moreover, the 1st electrode 2a, 2a, and 2a It intersects perpendicularly with the longitudinal direction of 2nd electrode 2b formed previously, it is prepared so that it may be crossed and located on edge section 1a of the above-mentioned insulating substrate 1 from on 2nd [ of a parenthesis ] electrode 2b, and it can prevent un-arranging [ which wiring from the 1st electrode and 2nd electrode short-circuits by this ]. Moreover, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed if needed on the 1st electrode 2a, 2a, and 2a and the fullerene thin film 3. Thus, the constituted semiconductor device can be used effective in an independent rectifying device, a transistor, a photosensor, etc.

[0019] In addition, the semiconductor device of this invention is not limited to the configuration of the above-mentioned example, and various gestalten are possible for it and it may consist of a crystal, powder, etc. Furthermore, various gestalten can be taken by the purpose of using a semi-conductor, and based on these purposes, the configuration of an electrode and a component is changed suitably and it deals in it.

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**EXAMPLE**

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[Example] (Example 1 of reference)

The semiconductor device which has the configuration shown in drawing 1 was produced. On slide glass 1, gear-tooth electrode 2a of a comb with gap width of face of 0.10mm, ten electrode overlap, and an electrode overall length of 50mm and 2b were formed with vacuum deposition. Gold was used for electrode 2a and 2b, and it stuck to the thickness of 500Å under the vacuum of  $5 \times 10^{-5}$  torr. The slide glass 1 in which this electrode 2a and 2b were formed was put on 20cm on the alumina crucible of a vacuum deposition machine, and it vapor-deposited, having put the carbon cluster C60 into the crucible made from an alumina, and heating at 520–550 degrees C under the vacuum of  $5 \times 10^{-6}$  torr (5Å/(second)), the vacuum deposition film 3 of C60 was stuck to the thickness of 300Å, and the semiconductor device was produced. They are wavelength;400nm and optical on-the-strength;7 mW/cm<sup>2</sup>, impressing the electric field of 10V to this component. When the homogeneous light was irradiated, the photocurrent of 55pA was detected. It is optical reinforcement 0.1, 0.5, 1.0 and 2.0, and 5.0 mW/cm<sup>2</sup> When it was made to change, the photocurrent also increased along with the increment in optical reinforcement. Subsequently, although this component was left for one month in atmospheric air, it was changeless to a photocurrent. Moreover, although the Scotch tape was stretched on the vacuum deposition film of C60 and subsequently being removed, C60 vacuum-deposition film has arrived at the substrate firmly, and did not separate. Furthermore, although the epoxy resin performed the protection coat on the front face of this component, it was almost changeless to a photocurrent. Therefore, the component obtained in this example of reference had the engine performance which was excellent as a photosensor.

[0021] (Example 1 of a comparison)

Like the above-mentioned example 1 of reference, on electrode 2a formed on slide glass 1, and 2b, vacuum deposition of the non-metal phthalocyanine was similarly carried out instead of the carbon cluster C60, and the thin film 3 was formed. When the same homogeneous light as the example 1 of reference was irradiated, the photocurrent of 15nA was observed. However, when this component was left for one month in atmospheric air, the photocurrent fell clearly. Moreover, when the Scotch tape was stuck and having been stripped on the non-metal phthalocyanine vacuum evaporation film, the thin film of a non-metal phthalocyanine peeled altogether with the Scotch tape. Furthermore, when a protection coat is carried out with an epoxy resin, most photocurrents are no longer observed by the fatal thing.

[0022] (Example 1)

In the example 1 of reference, the semiconductor device was similarly produced as electrode 2a and 2b except using aluminum instead of gold. When the homogeneous light as well as the example 1 of reference was irradiated, the photocurrent of 600pA was observed. The photocurrent was observed even if it changed the wavelength of the homogeneous light with 300,500,600,700nm. Therefore, it was admitted that this component could detect a photocurrent in a visible region from ultraviolet. Furthermore, when applied voltage was set to 100V, it was admitted by a photocurrent's becoming 10 times and impressing large electric field that an optical large response was obtained.

[0023]

## [0024] (Example 2)

The semiconductor device was produced in the above-mentioned example 1, using the cast film as a fullerene thin film 3. Like the example 1, using the spinner, the liquid made to dissolve the carbon cluster C60 in toluene was dropped, the cast film 3 of C60 was produced, the vacuum drying was carried out and the semiconductor device was produced at 100 more degrees C for 1 hour on electrode 2a which vapor-deposited aluminum on slide glass 1, and 2b. 1V are impressed to this component and they are 400nm and 5 mW/cm<sup>2</sup>. When the homogeneous light was irradiated, the photocurrent of 425pA was observed.

## [0025] (Example 3)

The semiconductor device which has the configuration shown in drawing 4 was produced. Width of face of 0.5cm and die length of 3cm were etched with the hydrochloric acid on 3cm 2cmx indium tin glass (ITO glass) 1, the conductive film was removed (part equivalent to 1in drawing 4 a), and the conductive remaining film was made into indium oxide (ITO) electrode 2b. On this electrode 2b, the polymer distribution film 3 of C60 was produced for the dispersion liquid (60; 20mg of C, vinyl acetate; 20mg, ethyl acetate; dispersion liquid which put the glass bead into 200mg and were distributed with the paint shaker for 1 hour) which made vinyl acetate / ethyl-acetate solution distribute C60 using bar coating-machine #10. The vacuum drying of this film 3 was carried out at 100 degrees C for 1 hour. Thickness was 1 micrometer. Subsequently, aluminum (width-of-face [ of 0.5cm ], die length of 1.5cm) electrode 2a was formed with three pieces and vacuum deposition on this film 3. From the function generator, the triangular wave of -2V to +2V was impressed at a scanning speed of 0.001Hz between this indium oxide electrode 2b and aluminum electrode 2a. The current-voltage characteristic at this time was shown in drawing 5 . The rectifying action was shown so that clearly from drawing 5 . On this component, although 3 sets of electrodes were formed, the repeatability was good. Moreover, even if it carried out the protection coat of the whole with the epoxy resin, the current-voltage characteristic hardly changed. Therefore, it was admitted that this component was an outstanding rectifying device.

## [0026] (Example 4)

In the above-mentioned example 3, except having replaced with the indium oxide electrode and having prepared tin-oxide electrode 2b by using NESA glass instead of ITO glass, when the semiconductor device was produced similarly, this thing showed the good rectifying action like the thing of an example 3.

## [0027] (Example 2 of a comparison)

In the above-mentioned example 3, the semiconductor device was similarly formed except using a non-metal phthalocyanine instead of C60. Also in this case, the rectifying action was shown similarly. However, when a protection coat was carried out with an epoxy resin, the rectifying action decreased greatly.

## [0028] (Example 5)

The semiconductor device which has the configuration shown in drawing 4 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, and on this substrate 1, vacuum deposition of the aluminum was carried out to the thickness of a 200 Å to 1000 Å, and it considered as electrode 2b (permeability of the 400nm homogeneous light; 2.18%). Furthermore, on this, vacuum deposition of C60 was carried out to 1000 Å thickness like the example 1 of reference, and the vacuum deposition film 3 of C60 was formed. Subsequently, on it, vacuum deposition of the two a3 0.5cmx1.5cm aluminum electrodes was carried out, and the semiconductor device was formed. When the triangular wave which is -1V to +1V was impressed to this component from the function generator (scanning speed; 0.002Hz), the current-voltage characteristic showed the bidirectional rectifying action as shown in drawing 6 . Moreover, repeatability was good about three electrodes.

## [0029] (Example 3 of a comparison)

2000 Å of alpha-sesquithienyls was vapor-deposited on the top face of the glass plate 1 in which aluminum electrode 2b was formed, like the example 5 (20 Å/(second)). If it is very hard to vapor-deposit alpha-sesquithienyl and it is vapor-deposited slowly, it will serve as film which decomposed and contained many impurities. Although decomposition will decrease if it vapor-

deposits quickly (20A/(second) or more), an impurity is contained too. Subsequently, 0.5cmx1.5cm aluminum electrode 2a was prepared by three-piece vacuum evaporation. The triangular wave of -2 to +2V was impressed to this component from the function generator (0.002Hz). This component showed a rectifying action, or did not show it, and its repeatability was very bad.

[0030] (Example 6)

The homogeneous light of wavelength;400nm and on-the-strength;700 microwatt/cm<sup>2</sup> was irradiated from the glass plate 1 side at the electrode, impressing 0.1V to aluminum electrode 2a of the semiconductor device obtained in the example 5, and 2b. The photocurrent of 535nA was observed at this time. When changing the wavelength of exposure light, the photocurrent has been observed to the 800nm homogeneous light. Moreover, by the homogeneous light with a wavelength of 400nm, when changing optical reinforcement, the photocurrent also increased according to exposure light reinforcement. Moreover, repeatability was good about three electrodes.

[0031] (Example 7)

The semiconductor device which has the configuration shown in drawing 4 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, on this substrate 1, platinum was stuck by sputtering and platinum-electrode 2b was formed. Subsequently, the polycarbonate polymer distribution film 3 of C60 was formed with the spinner, and it dried. Subsequently, aluminum electrode 2a was formed with vacuum deposition. The rectifying action was observed when the triangular wave of +1V was impressed from -1 like the example 5.

[0032] (Example 8)

When the platinum vacuum evaporation film was replaced with the carbon-shadowing film in the above-mentioned example 7 and carbon-electrode 2b was prepared, the rectifying action was shown similarly.

[0033] (Example 9)

In the above-mentioned example 5, except using C70 instead of C60, similarly, when the semiconductor device was obtained and measured, the current-voltage characteristic showed the same bidirectional rectifying characteristic.

[0034] (Example 10)

In the example 7, silver electrode 2b was formed with vacuum deposition instead of the platinum electrode. This component showed the rectifying action like drawing 5 similarly. Moreover, the photocurrent was observed when on-the-strength 1 mW/cm<sup>2</sup> and the 450nm homogeneous light were irradiated from an aluminum electrode side.

[0035] (Example 11)

In the example 7, copper-electrode 2b was formed with vacuum deposition instead of the platinum electrode. This component showed the rectifying action like drawing 5 similarly. Moreover, the photocurrent was observed when on-the-strength 1 mW/cm<sup>2</sup> and the 450nm homogeneous light were irradiated from an aluminum electrode side.

[0036] (Example 12)

In the example 3, instead of ITO glass and an indium oxide electrode, when others were performed like the example 3 using what formed zinc-oxide electrode 2b by sputtering on the glass substrate 1, the same rectifying action was observed.

[0037] (Example 13)

The same component as an example 5 was formed. First, after forming aluminum electrode 2b on a substrate, it once took out in air and was left under the room temperature for 24 hours. Then, it put in in the vacuum evaporation system, vacuum deposition of C60 was carried out to 1000Å thickness like the example 5, and the vacuum deposition film 3 of C60 was formed. Then, two pieces were vapor-deposited for 0.5cmx1.5cm aluminum electrode 2a, one piece was vapor-deposited for the golden electrode, respectively, and the semiconductor device was formed. The permeability of electrode 2a (aluminum, gold) and 400nm homogeneous light of 2b was 2%. After component formation, also when the current-voltage characteristic of -1→+1V was measured immediately, and electrode 2a was any of aluminum and gold, a rectifying characteristic like drawing 5 was shown. Moreover, when 1V were impressed between electrode 2a and 2b, 2 was

irradiated at aluminum electrode 2b and the homogeneous light was irradiated at the wavelength of 400nm on the strength of 5mW/cm, as compared with the time of irradiating the same light as aluminum electrode 2a or golden electrode 2a, the about 25 times as many photocurrent as this was observed. When argon etching of this component was carried out from the electrode 2a side using ESCA and the presentation of the membranous thickness direction was analyzed, it was admitted that the aluminum oxide existed in the interface of C60 film 3 and aluminum electrode 2b.

[0038] (Example 2 of reference)

Commercial crude soot was refined and C60 and C70 were obtained. First, 4g (vacuum metallurgy incorporated company make) of crude soot containing fullerene was put into the extraction thimble, and it extracted by n-hexane;200ml for 24 hours using the Soxhlet extractor. Subsequently, the solvent was changed into mesitylene;200ml and the extract was performed for further 24 hours. When the first n-hexane solution was analyzed by liquid chromatography (silica gel - n-hexane), the ratio of C60:C70 is 9:1 and did not contain most of 70 or more C fullerene. The ratio of C60:C70 is about 6:4, and the mesitylene extract was carrying out variety content of the 70 or more C fullerene. n-hexane extract was condensed by the evaporator and 0.26g fullerene mixture was obtained. Using the ODS column, the mixed solvent of a 2-propanol / toluene;6/4 was used as the developing solution, and 0.21g and 0.02g of high grades C70 were obtained for the high grade C60 using inside low voltage preparative chromatograph. The mesitylene extract was condensed by the evaporator and mixed fullerene 0.13g was obtained. It isolated preparatively by the chromatograph similarly and mixture;0.01g of 60; 0.07g of high grades C, 70; 0.04g of high grades C, and other fullerene was obtained. Mixture contained C76, C78, C84, and fullerene with still larger molecular weight from GC-MS analysis.

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[Translation done.]

**\* NOTICES \***

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2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

[Drawing 1] It is what showed the semiconductor device of this invention, and an example of a circuit, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).

[Drawing 2] It is what showed the semiconductor device of this invention, and an example of a circuit, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).

[Drawing 3] It is what showed the semiconductor device of this invention, and an example of a circuit, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).

[Drawing 4] It is what showed the semiconductor device of this invention, and an example of a circuit, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).

[Drawing 5] It is the graph which showed the example of the current-voltage characteristic of the semiconductor device of this invention.

[Drawing 6] It is the graph which showed the example of the current-voltage characteristic of the semiconductor device of this invention.

**[Description of Notations]**

2a, 2b — An electrode, 3 — Fullerene thin film

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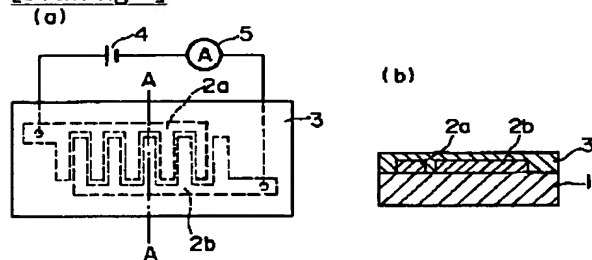
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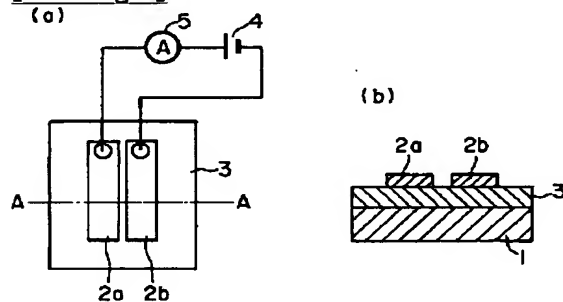
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## DRAWINGS

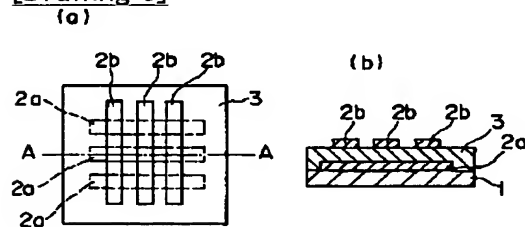
[Drawing 1]



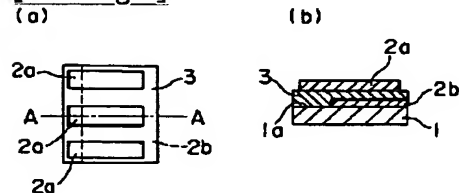
[Drawing 2]



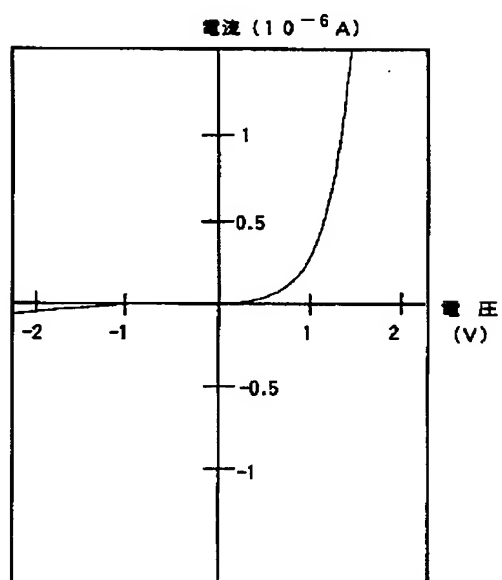
[Drawing 3]



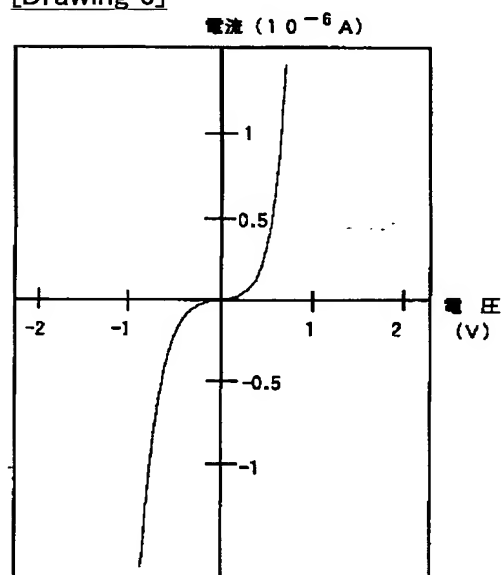
[Drawing 4]



[Drawing 5]



[Drawing 6]



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[Translation done.]



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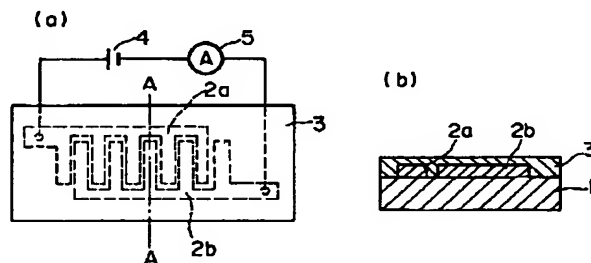
(54)【発明の名称】 半導体素子

(57)【要約】

【目的】 有機半導体素子で、改善された半導体素子、特に整流性および光センシング機能を有する半導体素子を提供する。

【構成】 本発明は有機物で構成される半導体素子であって、半導体としてフラーレン類、特にカーボンクラスターC60及びC70から成る群から選ばれた1種以上を用いて薄膜3を形成し、この薄膜に接するように電極2a、2bを設けて半導体素子を構成する。

【効果】 整流性、光センシング機能等を有するとともに、機械的強度に優れ、再現性の良い半導体素子が得られ、整流素子、トランジスター、光センサー等に有効に用いることができる。



## 【特許請求の範囲】

【請求項1】 フラーレン薄膜およびこれに接する2つ以上の電極を有してなることを特徴とする半導体素子。

【請求項2】 フラーレン薄膜が、カーボンクラスタで構成される薄膜であることを特徴とする請求項1記載の半導体素子。

【請求項3】 フラーレン薄膜が、カーボンクラスタC60および/またはカーボンクラスタC70で構成される薄膜であることを特徴とする請求項1または2のいずれかに記載の半導体素子。

【請求項4】 フラーレン薄膜が、真空蒸着膜、キャスト膜およびポリマー分散膜からなる群から選ばれる1種以上であることを特徴とする請求項1ないし3のいずれかに記載の半導体素子。

【請求項5】 電極が、金属電極、酸化物電極、および炭素電極からなる群から選ばれる1種以上であることを特徴とする請求項1ないし4のいずれかに記載の半導体素子。

【請求項6】 電極が、白金、金、銀、銅、アルミニウム、インジウム、酸化スズ、酸化インジウム、酸化亜鉛および炭素からなる群から選ばれる1種以上の材料からなる電極であることを特徴とする請求項5記載の半導体素子。

【請求項7】 少なくとも1つの電極がアルミニウム電極であることを特徴とする請求項6記載の半導体素子。

【請求項8】 アルミニウム電極がフラーレン薄膜との界面にアルミニウム酸化物層を有することを特徴とする請求項7記載の半導体素子。

【請求項9】 電極が、ギャップ電極またはサンドイッチ電極であることを特徴とする請求項1ないし8のいずれかに記載の半導体素子。

【請求項10】 半導体素子が、整流素子であることを特徴とする請求項1ないし9のいずれかに記載の半導体素子。

【請求項11】 半導体素子が、光センサーであることを特徴とする請求項1ないし9のいずれかに記載の半導体素子。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、有機半導体素子に係わり、特に優れた整流性および光導電性を有する半導体素子に関する。

## 【0002】

【従来の技術】 半導体素子の分野では、従来、硫化カドミニウム、酸化亜鉛、結晶シリコン、アモルファスシリコン、ガリウム砒素など無機物が使用されてきた。これらは、トランジスタ、整流素子、IC、LSI、光センサーおよび太陽電池等に使用されている。しかし、これらの無機物を用いて半導体素子を作製するためには、高度な真空装置、高度な製膜技術および高度な純度規制

等が要求され、容易にはなし得ないものであった。

【0003】 これに対し、有機物の多様性、半導体性等が注目されはじめ、ポリアセチレン、ポリピロール、フタロシアニン等の有機化合物の半導体性、導電性について多大な研究がなされてきた（「新・導電性高分子材料」、省部博之監修、シーエムシー、（1987））。特に、導電性高分子あるいは有機半導体を、金属で挟持してなる半導体素子として、ポリアセチレン、ポリジアセチレン、ポリピロール、 $\alpha$ -セスキエニル、フタロシアニン等の半導体薄膜（S）を金属電極（M）で挟持してなるMS素子、あるいは間に絶縁体の薄膜（I）を挟持してなるMIS素子等多くの素子が提案されている（「Physics of Semiconductor Devices」、2nd Edition、S.M.Sze、John Wiley & Sons、NY（1981）、D.Fichou、F.Garnier et al.、CHEMTRONICS、1988、176頁）。これらの有機化合物はP型あるいはN型の半導体性を示し、仕事関数の小さい電極と仕事関数の大きい電極で挟持したとき整流性を示す。例えば、 $\alpha$ -セスキエニルの場合（D.Fichou、F.Garnier et al.、CHEMTRONICS、1988、176頁）、これをアルミニウムとインジウムチンオキサイド（あるいは金）電極で挟持したとき $\pm 1$ Vで100倍以上の整流性を示す。さらに、異種導電性高分子の接合で、整流素子を構築した例（Pt|ポリピロール|ポリチフェン|In、M.Aizawa、H.Shirakawa、Synth.Met.、18号、711頁（1987））、FETを構築した例（H.Koezuka、et al.、Synth.Met.、18号、699頁（1987））も知られている。また、フタロシアニン等は光導電性を示し、太陽電池等への応用が検討され、アルミニウムおよびITOガラス（酸化インジウム～酸化スズ薄膜による導電性ガラス）で挟持した太陽電池が検討されている。

## 【0004】

【本発明が解決しようとする課題】 上記の有機化合物は一般にS層すなわち導電性高分子層あるいは有機半導体層の不安定性（ポリアセチレンに於ける空気、湿度等に対する不安定性、ドーピング後の不安定性等）、不純物の混入による再現性の低下（ $\alpha$ -セスキエニル、フタロシアニン等は濃硫酸程度しか溶解する溶媒が無く純度の向上が非常に困難である）、素子形成時の不確定性（気相重合、電解重合等による触媒、電解質等の混入等、 $\alpha$ -セスキエニル、フタロシアニン等の真空蒸着時の熱分解による不純物の混入）、素子形成後の電極の腐食（ドーパントによる電極の腐食、フタロシアニンに見られるようなアルミニウム電極の酸化促進等）、薄膜の機械的脆さ（ $\alpha$ -セスキエニル、フタロシアニン等の真空蒸着膜はこすると剥がれる）等によりいずれも実用化に至っていない。さらに太陽電池では、その経時劣化、変換効率の低さから実用化に至っていない。わずかに有機物で実用化されたものは、ポリアニリンを用いたポリマーバッテリー、TCNQを用いたコンデンサー、フタロシアニン等を用いた電子写真感光体程度であり、

見るべき成果がないのが現状である。

#### 【0005】

【課題を解決するための手段】本発明者らは、従来の導電性高分子をはじめとする有機半導体の上記の如き種々の欠点に鑑み、これらを改良すべく鋭意検討を行った結果、フラーレン薄膜を用い、これに接するように2つ以上の電極を設けることにより、容易に再現性よく半導体素子が得られ、前記課題も解決することができることを見出し、本発明を完成するに至った。

【0006】すなわち、本発明はフラーレン薄膜およびこれに接する2つ以上の電極を有してなることを特徴とする半導体素子を提供するものである。

【0007】以下、本発明を詳しく説明する。本発明で用いられるフラーレン薄膜は、フラーレン類を用いて形成された薄膜である。ここで、フラーレン類とは、sp<sup>2</sup>炭素よりなる球状あるいはラグビーボール状のカーボンクラスタの総称であり、一般にC<sub>60</sub>、C<sub>70</sub>、C<sub>76</sub>、C<sub>78</sub>、C<sub>84</sub>等が知られている。これらは、炭素をアーク放電あるいは抵抗加熱して気化させ、ヘリウム等の不活性ガスで急冷して生成したすすの中等に含有され（例えば、Kraetschmer等、Nature、347号、354頁(1990)等）、C<sub>60</sub>が最も多く含有されている。そしてこのすすから、例えばヘキサン、ベンゼン、トルエン、メシチレン、二硫化炭素等の溶媒で抽出することによって上記カーボンクラスタの混合物が得られる。さらにこの混合物を精製し、各々単離するには、通常有機化合物の精製に用いられるクロマトグラフィーの手法（例えば、Kraetschmer等、Nature、347号、354頁(1990)等）を用いることができる。本発明においては、合成、単離が容易なC<sub>60</sub>またはC<sub>70</sub>、あるいはこれらを含有するすすから抽出、不溶性不純物除去を施して得られる混合フラーレンが好ましく用いられる。

【0008】フラーレン薄膜は各種の製膜方法により形成して用いることができ、例えば真空蒸着膜、キャスト膜およびポリマー分散膜等を用いることができる。真空蒸着膜は、例えば一般的真空蒸着の手法に従い（薄膜ハンドブック、日本学術振興会薄膜第131委員会編、オーム社（1984）等）、 $5 \times 10^{-5}$  torr以下の真空下で、金属性ボートあるいはアルミナ性ボートなどを用いてフラーレン類を加熱し、その上部あるいは下部に基板を置くことで薄膜を形成できる。この際、必要に応じ、基板を加熱あるいは冷却しても良い。基板を冷却した場合、薄膜はアモルファス状態となり、また、室温あるいはそれ以上に加熱した場合は結晶状態として得られる。このフラーレン類の真空蒸着膜は空気中で安定で、かつ非常に硬く強固である。例えば、従来のフタロシアニン、 $\alpha$ -セスキチエニル等はこすれば剥がれ、セロテープ等により簡単に剥離できるように機械的強度に劣るのに対し、フラーレン類の蒸着膜はこすってもなかなか剥がれず、セロテープでは剥離できない強固な膜で

あり、機械的強度に優れる。

【0009】キャスト膜は、例えばフラーレン類がベンゼン、トルエン、メシチレン等芳香族炭化水素、二硫化炭素、n-ヘキサン等に溶解する性質を利用するもので、簡便に薄膜を作成しうる手段である。すなわち上記溶媒等に溶解せしめ、基板上に滴下する、あるいは基板をスピナー上に固定し、上記溶解液を滴下した後、スピナーを適当な回転数で回転せしめ薄膜化する、あるいは基板上に滴下した溶液をバーコーターまたはドクターブレード等を用いて薄膜化するなどの手段で薄膜化し、次いで自然乾燥、あるいは熱または真空乾燥するなどの手段で乾燥することによって製膜することができる。

【0010】ポリマー分散膜は、例えばポリマーの溶液中にフラーレン類を添加し、溶解あるいは分散せしめた後、上記キャスト膜と同様の手段で製膜することができる。分散方法としては、ペイントシェーカー、スベックスマキサーミル、サンドミル、ボールミル、アトラクター、ニーダー等の顔料分散手法を用いることができる。ここで用いることができるポリマーとしては、特に制限はないが、例を挙げると、飽和ポリエステル、不飽和ポリエステル、ポリカーボネート、ポリ塩化ビニール、ポリ酢酸ビニール、ポリビニールカルバゾール、スチレン等のビニール系ポリマー、フッ化ポリビニリデン、フッ化ポリビニル等のフッ素化ポリマー、スチレン-マレイン酸等のコポリマー等がある。また、例えば、ポリアクリレート系液晶高分子、ポリシロキサン系液晶高分子等の液晶高分子を用いることもできる。

【0011】フラーレンの優れた半導体性を引き出すには、フラーレン薄膜に接する2つ以上の電極を設けることが必要である。電極としては、例えば金属電極、金属酸化物電極および炭素電極等を用いることができる。例えば、仕事関数の小さいリチウム、ベリリウム、ナトリウム、マグネシウム、アルミニウム、カリウム、インジウム、カルシウム、スカンジウム、チタン、マンガン、ジルコニウム、ガリウム、ニオブ、アンチモン等、または仕事関数の大きいパラジウム、テルル、レニウム、イリジウム、銅、銀、金、白金、ルテニウム、ゲルマニウム、酸化スズ（例えばネサガラス）、酸化インジウム、酸化インジウム-酸化スズ（例えばITOガラス）、酸化亜鉛、グラファイト、グラッシーカーボン、銀ペーストおよびカーボンペースト等が用いられるが、特に、白金、金、銀、銅、アルミニウム、インジウム、酸化スズ（例えばNESAGラス、NESACコートポリマー膜）、酸化インジウム（例えばITOガラス、ITOコートポリマー膜）、酸化亜鉛および炭素が好ましい。半導体素子、特にトランジスター、整流素子等として用いるときは、上記の仕事関数の小さい電極と仕事関数の大きい電極を設ける必要がある。但し、アルミニウム電極を用いるときは、本発明の半導体素子は特に双方向の整

流性を示し、双方向スイッチング素子、双方向整流素子等として使用することができる。さらに、アルミニウム電極を形成した後、この電極を空気に曝すと、表面に極薄いアルミニウム酸化物層が形成される。この上にフラーレン薄膜を形成し、次いで任意の電極を形成して構成された本発明の素子も、より高い整流比を示し、整流素子としてさらに望ましいものとなる。一方、光センサーとして用いるときは、電極はいずれの電極を用いてもよく、両極として作用するお互いの電極が異なってもよい。さらに、お互いの電極あるいは一方の電極にアルミニウムを用いるときは、より大きな光電流を得ることができる。特に、上記の如きアルミニウム酸化物層を電極とフラーレン薄膜との界面に形成して得た素子では、さらに大きな光電流を得ることができ、好ましいものとなる。

【0012】電極は、例えば金属板、炭素板、薄膜、導電性塗料膜等いずれの形態でも使用する事ができる。薄膜の形態で使用する時、金属箔、蒸着膜、スパッタリング膜、電着膜、スプレー熱分解膜等の手段で薄膜化して使用することができる。また、導電性塗料（例えば銀、炭素含有塗料）を塗布して電極を形成することもできる。ここで、製膜あるいは塗布によって電極を設ける場合には、半導体素子は基板を用いて好ましく形成される。この基板としては特に制限はなく、絶縁性のものであれば良い。また、金属板、炭素板等板状の電極を用いるときは、特に基板を用いなくても良い。

【0013】電極の構成としては、例えば平行電極あるいは櫛の歯電極等のギャップ電極、またはフラーレン薄膜を挟むように設けられるサンドイッチ電極等を用いることができる。半導体素子、特に整流素子として使用するとき、あるいはギャップ電極で光センサーとして使用するとき、電極の膜厚は任意とすることができる。また、ギャップ電極のギャップ幅は特に制限はないが、ギャップ幅が大きいと電流が小さくなるので、1mm以下のギャップが好ましい。また、ギャップ長は長い方が、電流値が大きくなり、大きな応答が得られるので好適である。ギャップ電極のなかでも、櫛の歯電極を用いると、ギャップ長が更に長くできるのでより好ましい。これに対してサンドイッチ電極で光センサーとして使用するとき、光を入射する側の電極は半透明である必要がある。酸化物電極を用いるときは、光の透過率が98%～0.1%の範囲が用いられるが、光の透過率が大きい方が光に対する応答性は高い。金属電極の場合、光の透過率が大きい方が光に対する応答性は高いが、透過率が大きすぎると電極が電流を通さない。従って、光の透過率は50%～0.1%の範囲が好適に用いられる。

【0014】また半導体素子を構成するフラーレン薄膜の膜厚については、ギャップ電極を用いる場合は、最低1分子の厚みがあれば良く、10オングストローム～100μmの範囲で用いることができ、特に10オングス

トローム～10μmの範囲が特に好適に用いられる。サンドイッチ電極を用いる場合は、薄すぎるとお互いの電極が短絡するので、ある程度の厚さが必要である。この場合、フラーレン薄膜の膜厚は100オングストローム～100μmの範囲が好適であり、特に好ましくは、200オングストローム～10μmに形成される。

【0015】以上説明したようなフラーレン薄膜および電極を用いて構成される本発明の半導体素子を図面を用いて説明する。図1～4はいずれも本発明の半導体素子の一例を示したものである。図1および図2はいずれもギャップ電極を用いた半導体素子と回路の一例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。図中符号1は絶縁基板、2a、2bは電極、3はフラーレン薄膜、4は直流電源、5は電流計である。図1に示した半導体素子は絶縁基板1上に2つの櫛の歯電極2a、2bが、僅かのギャップを有して噛合するように設けられ、さらにその上面にフラーレン薄膜3が形成されている。また、電極2a、2bは直流電源4および電流計5を介して接続されている。さらに必要に応じて、フラーレン薄膜3を覆う絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。あるいは、図2(b)のように絶縁基板1上にフラーレン薄膜3を形成し、さらにその上面に櫛の歯電極2a、2bを設けた構成とすることもできる。このようなギャップ電極を用いた半導体素子は、光センサーとして好適に用いることができ、電極2a、2bに電源4から電場を印加した状態で、フラーレン薄膜3に光が照射されると、電極2a、2b間の電流値が変化する。この電流値の変化量は電流計5によって検出され、これに基づいて照射された光強度を測定することができる。

【0016】図2にギャップ電極を用いた本発明の半導体素子と回路の他の例を示す。この例の半導体素子は、絶縁基板1上にフラーレン薄膜3が形成され、その上面に2つの平行電極2a、2bが設けられている。さらに必要に応じて、電極2a、2bおよびフラーレン薄膜3を覆う絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。あるいは、図1(b)のように絶縁基板1上に平行電極2a、2bを設け、その上面にフラーレン薄膜3を形成した構成とすることもできる。

【0017】図3および図4はサンドイッチ電極を用いた半導体素子の例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。図3に示した半導体素子は、絶縁基板1上に、短冊状に形成された3つの第1の電極2a、2a、2aが平行に設けられ、絶縁基板1およびこれら第1の電極2a、2a、2aの上面にフラーレン薄膜3が形成され、さらにこのフラーレン薄膜3上に短冊状に形成された3つの第2の電極2b、2b、2bが平行に、かつ上記第1の電極2

a, 2a, 2aと直交するように設けられている。さらに必要に応じて、第2の電極2b, 2b, 2bおよびフラーレン薄膜3を覆う絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。ここで、第1の電極および第2の電極の数は、それぞれ1以上の任意の数に設定することができる。このようなサンドイッチ電極を用いた半導体素子は、集積化した整流素子（例えばスイッチング素子等）に好適に用いられ、例えば、液晶、ECD等の駆動を行うことができる。または、光センサー（例えばイメージセンサー等）としても好適に用いられる。これらの場合、外部駆動装置（図示せず）から互いに直行する第1の電極および第2の電極に電場を印加して、整流素子あるいは光センサーとして用いることができる。

【0018】図4はサンドイッチ電極を用いた本発明の半導体素子の他の例を示したものである。このものは絶縁基板1上に、第2の電極2bが設けられ、この絶縁基板1および第2の電極2b上全面にフラーレン薄膜3が形成され、さらにフラーレン薄膜3上には、短冊状に形成された第1の電極2a, 2a, 2aが設けられている。この第1の電極2aの数は、1以上の任意の数に設定することができる。尚、第1の電極2aは、短冊状だけでなく、円、楕円等いかなる形状でもよい。また、第2の電極2bは、基板1上面の一方の端縁部1aを残して太い帯状に形成され、第1の電極2a, 2a, 2aは、先に形成した第2の電極2bの長手方向に直交し、かつこの第2の電極2b上から上記絶縁基板1の端縁部1a上に渡って位置するように設けられ、このことにより第1の電極および第2の電極からの配線が短絡する不都合を防止することができる。また必要に応じ、第1の電極2a, 2a, 2aおよびフラーレン薄膜3上に絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。このように構成された半導体素子は、単独の整流素子、トランジスター、光センサー等に有効に用いることができる。

【0019】尚、本発明の半導体素子は、上記実施例の構成に限定されるものではなく、種々の形態が可能であり、結晶、粉末等で構成されても良い。更に、半導体の使用目的により種々の形態をとることができ、これらの目的に基づき、電極および素子の構成は適宜変更されるものである。

#### 【0020】

【実施例】（実施例1）図1に示した構成を有する半導体素子を作製した。スライドガラス1上に、ギャップ幅0.10mm、電極オーバーラップ10個、電極全長50mmの櫛の歯電極2a, 2bを真空蒸着により形成した。電極2a, 2bには金を使用し、 $5 \times 10^{-5}$  torrの真空中で500オングストロームの厚さに着けた。この電極2a, 2bを形成したスライドガラス1を真空蒸着器のアルミナルツボ上20cmに置き、カーボンク

ラストC60をアルミナルツボに入れ $5 \times 10^{-6}$  torrの真空中で520～550℃に加熱しながら蒸着し（5オングストローム/秒）、C60の真空蒸着膜3を300オングストロームの厚さに着け、半導体素子を作製した。この素子に10Vの電場を印加しながら、波長；400nm、光強度；7mW/cm<sup>2</sup>の単色光を照射したところ、55pAの光電流が検出された。光強度を0.1、0.5、1.0、2.0、5.0mW/cm<sup>2</sup>と変化させたとき、光強度の増加につれ、光電流も増加した。次いで、この素子を大気中に1ヶ月間放置したが、光電流に変化はなかった。また、C60の真空蒸着膜上にセロテープをはり、ついで剥がしたが、C60真空蒸着膜は強固に基板に着いており、剥がれなかった。更に、この素子の表面にエポキシ樹脂で保護コートを行ったが、光電流にほとんど変化はなかった。従って、本実施例で得られた素子は、光センサーとして優れた性能を有していることが認められた。

【0021】（比較例1）上記実施例1と同様にして、スライドガラス1上に形成した電極2a, 2b上に、カーボンクラスターC60の代わりに無金属フタロシアニンを同様にして真空蒸着し、薄膜3を形成した。実施例1と同様の単色光を照射したところ、15nAの光電流が観測された。しかしながら、この素子を大気中に1ヶ月間放置したところ、光電流は明らかに低下した。また、無金属フタロシアニン蒸着膜上にセロテープを貼り、はがしたところ、無金属フタロシアニンの薄膜はセロテープとともに全てはがれた。更に致命的なことには、エポキシ樹脂で保護コートしたところ、光電流はほとんど観測されなくなった。

【0022】（実施例2）実施例1において、電極2a, 2bとして、金の代わりにアルミニウムを使用する以外は同様にして、半導体素子を作製した。実施例1と同様にして単色光を照射したところ、600pAの光電流が観測された。単色光の波長を300, 500, 600, 700nmと変化させても、光電流は観測された。したがって、本素子は、紫外から可視領域におよんで光電流を検出できることが認められた。更に、印加電圧を100Vとすると、光電流は10倍となり、大きい電場を印加することにより、大きい光応答が得られることが認められた。

【0023】（実施例3）図2に示した構成を有する半導体素子を作製した。スライドガラス1上に、すすから抽出し、クロマトグラフィーで、不溶物を除去したフラーレン混合物（液体クロマトグラフィー分析ではC60を80%、C70を19%含有し、残り1%はC70以上の高次のフラーレン化合物であった）を用いて100オングストロームの厚さに真空蒸着し、フラーレン薄膜3を形成した。ついで、ギャップ幅10μm、長さ10mmのインジウム電極2a, 2bを真空蒸着により形成して半導体素子を作製した。ギャップ電極に10Vの

電場を印加し、波長400nm、強度5mW/cm<sup>2</sup>の単色光を照射したところ、400pAの光電流が観測された。

【0024】（実施例4）上記実施例2において、フーレン薄膜3としてキャスト膜を用いて半導体素子を作製した。実施例2と同様にして、スライドガラス1上にアルミニウムを蒸着した電極2a、2b上に、カーボンクラスタC60をトルエンに溶解させた液を滴下し、スピナーを用いて、C60のキャスト膜3を製膜し、さらに100℃で、1時間、真空乾燥して半導体素子を作製した。この素子に1Vを印加し、400nm、5mW/cm<sup>2</sup>の単色光を照射したところ、425pAの光電流が観測された。

【0025】（実施例5）図4に示した構成を有する半導体素子を作製した。2cm×3cmのインジウムスズガラス（ITOガラス）1上において、幅0.5cm、長さ3cmを塩酸でエッチングして導電性膜を除去（図4中1aに相当する部分）し、残りの導電性膜を酸化インジウム（ITO）電極2bとした。この電極2b上に、C60を酢酸ビニル/酢酸エチル溶液に分散させた分散液（C60；20mg、酢酸ビニル；20mg、酢酸エチル；200mgにガラスビーズを入れペイントシェーカーで1時間分散した分散液）をバーコーター#10を用いてC60のポリマー分散膜3を製膜した。この膜3を100℃で1時間、真空乾燥した。膜厚は、1μmであった。ついで、この膜3上にアルミニウム（幅0.5cm、長さ1.5cm）電極2aを3個、真空蒸着により形成した。この酸化インジウム電極2bとアルミニウム電極2aの間に-2Vから+2Vの三角波をファンクションジェネレータより、0.001Hzのスキュンスピードで印加した。この時の電流-電圧特性を図5に示した。図5から明らかなように、整流性を示していた。本素子上、3組の電極が形成されているが、その再現性は良好であった。また、エポキシ樹脂で、全体を保護コートしても電流-電圧特性はほとんど変化しなかった。したがって、本素子は優れた整流素子であることが認められた。

【0026】（実施例6）上記実施例5において、ITOガラスの代りにNESAガラスを用いることによって、酸化インジウム電極に代えて酸化スズ電極2bを設けた以外は同様にして半導体素子を作製したところ、このものは実施例5のものと同様に良好な整流性を示した。

【0027】（比較例2）上記実施例5において、C60の代わりに無金属フタロシアニンを用いる以外は同様にして、半導体素子を形成した。この場合も同様に整流性を示した。しかし、エポキシ樹脂で保護コートしたとき、整流性は大きく減少した。

【0028】（実施例7）図4に示した構成を有する半導体素子を作製した。2cm×3cmのガラス基板1の

上部0.5mm×3cmを遮蔽し、この基板1上にアルミニウムを200オングストロームの厚さに真空蒸着して電極2bとした（400nmの単色光の透過率；2.18%）。さらにこの上に実施例1と同様にしてC60を1000オングストロームの膜厚に真空蒸着し、C60の真空蒸着膜3を形成した。ついで、その上に0.5cm×1.5cmのアルミニウム電極2a3個を真空蒸着し、半導体素子を形成した。この素子に-1Vから+1Vの三角波をファンクションジェネレータから印加した（スキュンスピード；0.002Hz）ところ、電流-電圧特性は図6に示すような双方向の整流性を示した。また、3個の電極について再現性は良好であった。

【0029】（比較例3）実施例7と同様にして、アルミニウム電極2bを形成したガラス板1の上面に、α-セスキエニルを2000オングストローム蒸着した（20オングストローム/秒）。α-セスキエニルは、非常に蒸着しづらく、ゆっくり蒸着すると、分解し不純物を多く含んだ膜となる。速く（20オングストローム/秒以上）蒸着すれば分解は少なくなるが、やはり不純物を含有する。ついで、0.5cm×1.5cmのアルミニウム電極2aを3個蒸着により設けた。この素子に、-2から+2Vの三角波をファンクションジェネレータから印加した（0.002Hz）。この素子は、整流性を示したり、示さなかったりし、再現性が非常に悪かった。

【0030】（実施例8）実施例7で得られた半導体素子のアルミニウム電極2a、2bに0.1Vを印加しながら、ガラス板1側から、電極に波長；400nm、強度；700μW/cm<sup>2</sup>の単色光を照射した。この時、535nAの光電流が観測された。照射光の波長を変化させたとき、光電流は800nmの単色光まで、観測できた。また、400nmの波長の単色光で、光強度を変化させたとき、照射光強度に応じて、光電流も増加した。また、3個の電極について再現性は良好であった。

【0031】（実施例9）図4に示した構成を有する半導体素子を作製した。2cm×3cmのガラス基板1の上部0.5mm×3cmを遮蔽し、この基板1上に白金をスパッタリングで着け、白金電極2bを形成した。ついでC60のポリカーボネートポリマー分散膜3をスピナーで形成し、乾燥した。ついで、アルミニウム電極2aを真空蒸着で形成した。実施例7と同様に-1から+1Vの三角波を印加したところ、整流性が観測された。

【0032】（実施例10）上記実施例9において白金蒸着膜をカーボン蒸着膜に代えて、炭素電極2bを設けたところ、同様に整流性を示した。

【0033】（実施例11）上記実施例7において、C60の代わりにC70を用いる以外は同様にして、半導体素子を得、測定したところ、電流-電圧特性は同様の双方向の整流特性を示した。



【0034】（実施例12）実施例9において、白金電極の代わりに、銀電極2bを真空蒸着により形成した。この素子も同様に図5の如くの整流性を示した。また、アルミニウム電極側より強度1mW/cm<sup>2</sup>、450nmの単色光を照射したとき、光電流が観測された。

【0035】（実施例13）実施例9において、白金電極の代わりに、銅電極2bを真空蒸着により形成した。この素子も同様に図5の如くの整流性を示した。また、アルミニウム電極側より強度1mW/cm<sup>2</sup>、450nmの単色光を照射したとき、光電流が観測された。

【0036】（実施例14）実施例5において、ITOガラスおよび酸化インジウム電極の代わりに、ガラス基板1上に酸化亜鉛電極2bをスパッタリングで形成したものを、その他は、実施例5と同様に行ったところ、同様の整流性が観測された。

【0037】（実施例15）実施例7と同様な素子を形成した。まず、基板上にアルミニウム電極2bを形成した後、一旦空気中に取り出し、室温下に24時間放置した。その後、真空蒸着装置内に入れ、実施例と同様にしてC60を1000オングストロームの膜厚に真空蒸着しC60の真空蒸着膜3を形成した。引き続き、0.5cm×1.5cmのアルミニウム電極2aを2個、金電極を1個をそれぞれ蒸着し、半導体素子を形成した。電極2a（アルミニウム、金）、2bの400nm単色光の透過率は2%であった。素子形成後、直ちに-1〜+1Vの電流-電圧特性を測定したところ、電極2aがアルミニウム、金のいずれの場合にも図5のような整流特性を示した。また、電極2aと2bの間に1Vを印加し、アルミニウム電極2bに強度5mW/cm<sup>2</sup>、波長400nmに単色光を照射したところ、アルミニウム電極2aあるいは金電極2aに同様の光を照射したときに比して約25倍の光電流が観測された。本素子をESCAを用いて、電極2a側からアルゴンエッチングして、膜の厚さ方向の組成を分析したところ、C60膜3とアルミニウム電極2bとの界面にアルミニウム酸化物が存在しているのが認められた。

【0038】（参考例）市販の粗製すすを精製してC60およびC70を得た。まず、フラーレン類を含有する粗製すす（真空冶金株式会社製）4gを円筒濾紙に入れ、ソックスレー抽出器を用い、n-ヘキサン；200mlで24時間抽出した。ついで、溶媒をメシチレン；200mlに変更し、更に24時間抽出を行った。初めのn-ヘキサン溶液を液体クロマトグラフィ（シリカゲル〜n-ヘキサン）で分析したところ、C60：C70の比は9：1であり、C70以上のフラーレンをほとんど含有していなかった。メシチレン抽出液は、C60：C70の比は約6：4であり、C70以上のフラーレンを多種含有していた。n-ヘキサン抽出液をエバポレータで濃縮し、0.26gのフラーレン混合物を得た。O

DSカラムを用い、2-プロパノール／トルエン；6／4の混合溶媒を展開液とし、中低圧分取クロマトグラフを用いて、高純度C60を0.21g、高純度C70を0.02g得た。メシチレン抽出液をエバポレータで濃縮し、混合フラーレン0.13gを得た。同様にクロマトグラフで分取して、高純度C60；0.07g、高純度C70；0.04g、その他フラーレン類の混合物；0.01gを得た。混合物は、GC-MS分析からC76、C78、C84および更に分子量の大きいフラーレン類を含有していた。

【0039】

【発明の効果】以上説明したように、本発明の半導体素子は、フラーレン薄膜およびこれに接する2つ以上の電極を有してなるものである。この発明の半導体装置は、半導体性、特に整流性、光導電性を示すものである。そしてフラーレン類は、合成が容易で、かつ溶媒に溶解するため、精製が容易で高純度品を容易に得ることができる。また、耐熱性も高く、蒸着時の分解も起こらないため、素子化が容易で、再現性の良い特性が得られる。また、真空を必要としないキャスト膜、ポリマー分散膜の形で使用できる。したがって、フラーレン類を製膜して得られるフラーレン薄膜を用いることによって、安定性、再現性に富む半導体素子を容易に構成することができる。さらに、本発明の半導体素子は樹脂等を用いた保護コートを実施しても性能が変化しない為、広範な用途に用いることができる。特に、整流素子、整流性を用いた液晶、ECD素子等の駆動素子、光センサー、あるいは光センサー機能を応用したイメージセンサー等に幅広く応用することができる。

【図面の簡単な説明】

【図1】 本発明の半導体素子と回路の一例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。

【図2】 本発明の半導体素子と回路の一例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。

【図3】 本発明の半導体素子と回路の一例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。

【図4】 本発明の半導体素子と回路の一例を示したもので、(a)は平面図、(b)は(a)中のA-A線に沿う断面図である。

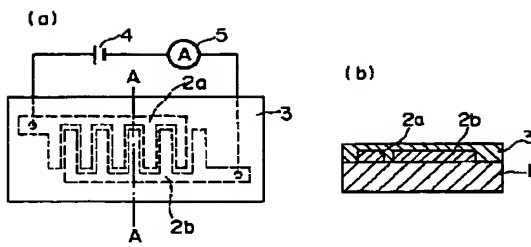
【図5】 本発明の半導体素子の電流-電圧特性の例を示したグラフである。

【図6】 本発明の半導体素子の電流-電圧特性の例を示したグラフである。

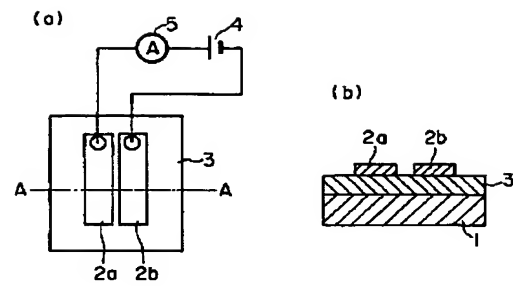
【符号の説明】

2a, 2b…電極、3…フラーレン薄膜

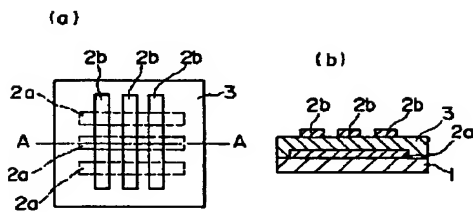
【図1】



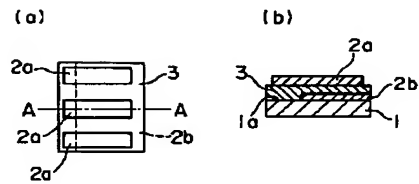
【図2】



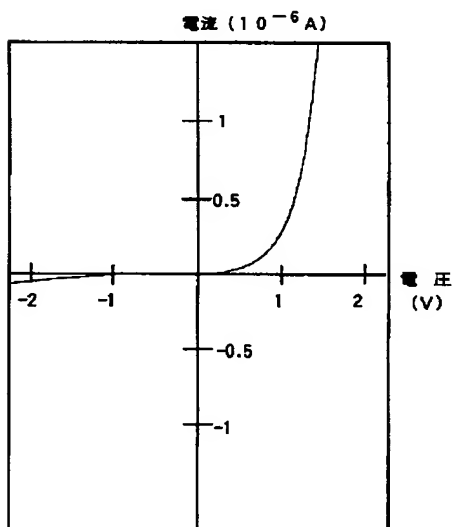
【図3】



【図4】



【図5】



【図6】

